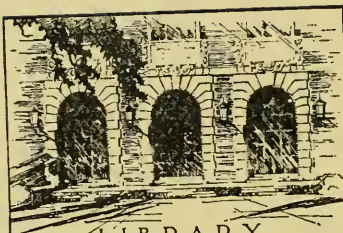


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A. V. BLEININGER, Director

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## COBALT COLORS OTHER THAN BLUE

BY  
R. T. STULL AND G. H. BALDWIN

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## INFLUENCES OF VARIABLE SILICA AND ALUMINA ON PORCELAIN GLAZES OF CONSTANT RO

BY  
R. T. STULL

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## INVESTIGATIONS ON THE DIELECTRIC STRENGTH OF SOME PORCELAINS

BY  
B. S. RADCLIFFE

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1911-1912

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## COBALT COLORS OTHER THAN BLUE.

By R. T. STULL and G. H. BALDWIN, Ceramic Laboratories,  
University of Illinois.

### INTRODUCTION.

The color imparted to a glass or glaze depends upon the kind of coloring oxide, the composition of the batch and the manner of heat treatment. It has been considered that cobalt is persistent in producing blue under all conditions. Since two or more distinct colors are obtainable from all other coloring oxides under different conditions, there seemed to be no logical reason why some color other than blue could not be obtained from cobalt oxide.

Since cobalt oxide has so persistently given blue colors under normal ceramic practice, it was evident that a departure in composition must be made from the ordinary commercial types of glazes if a color different from blue was to be developed from cobalt oxide.

A speculation as to the possible colors obtainable from cobalt oxide as the sole colorant is of interest. Cobalt salts in solution under certain conditions impart pink, while under other conditions the color imparted is blue. It, therefore, seemed possible to develop all the different shades from blue on one hand to pink or even light red on the other. The problem was to develop a type of glaze that would bring out the pink or red color if such were possible, and the key to the situation was found in blowpipe analysis. Magnesia and magnesium minerals containing cobalt, when powdered, moistened with a solution of cobalt nitrate and heated, give a pink color. Alumina and alumina minerals containing cobalt, when similarly treated, give blue.

This suggested a glaze high in magnesia and free from alumina. It was recognized that if such colors could be produced they would be of greatest value for low temperature work. Since a high content of magnesia imparts refractoriness to a glaze, it would be necessary to introduce a "softener" which would not influence the color toward the blue. Of the two "softeners,"  $PbO$  and  $B_2O_3$ , tried in a preliminary test,<sup>1</sup> it was found that the

<sup>1</sup> Vol. XII, Trans. A. C. S., pp. 707-708.

former changed the magnesia-cobalt pink to blue, while the latter did not, hence  $B_2O_3$  was selected as the "fluxing" or "softening" agent.

#### EXPERIMENTAL WORK.

**First Group.**—The first group of glazes was made in order to develop workable members over a range of temperatures. In this group the RO remained constant, the  $SiO_2$  and  $B_2O_3$  being variables. The limits covered were

$$\left. \begin{array}{l} 0.2 \text{ Na}_2\text{O} \\ 0.6 \text{ MgO} \\ 0.2 \text{ CoO} \end{array} \right\} 0 \text{ to } 1.0 \text{ B}_2\text{O}_3, \quad 1.0 \text{ to } 4.0 \text{ SiO}_2.$$

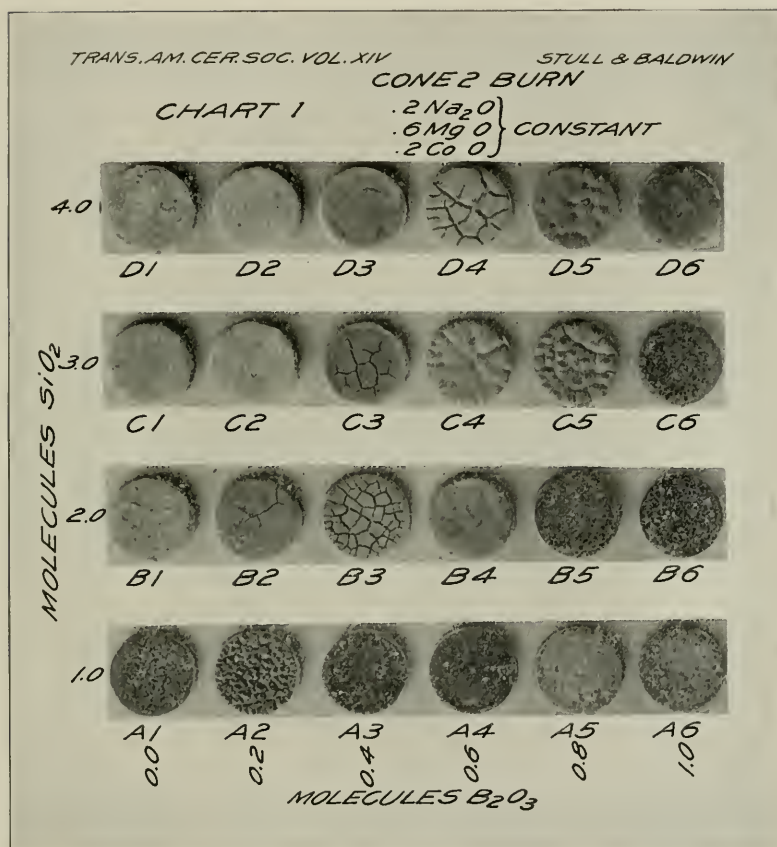
Twenty-four glazes were made in this group. The horizontal series are designated by letters and the vertical series by numbers (see charts). The formula and batch weights of the four corner glazes are:

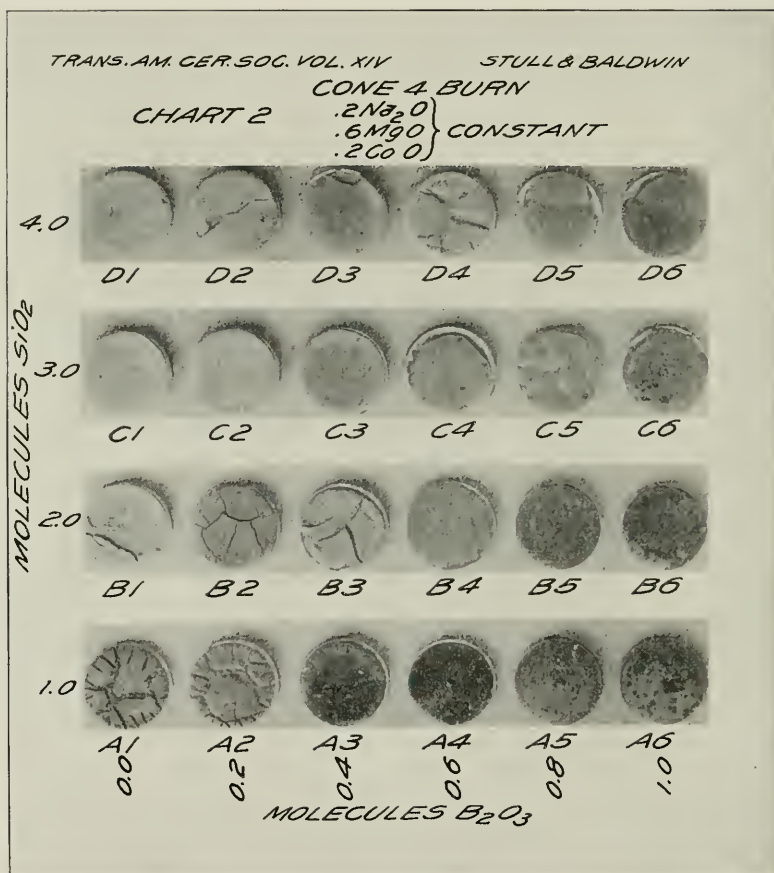
	Formulae					Batch weights				
	Na <sub>2</sub> O	MgO	CoO	B <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>	MgCO <sub>3</sub>	Co <sub>2</sub> O <sub>3</sub>	B <sub>2</sub> O <sub>3</sub> ·3H <sub>2</sub> O	Flint
A-1.....	0.2	0.6	0.2	0	1.0	212	504	165	..	600
A-6.....	0.2	0.6	0.2	1.0	1.0	212	504	165	1240	600
D-1.....	0.2	0.6	0.2	0	4.0	212	504	165	..	2400
D-6.....	0.2	0.6	0.2	1.0	4.0	212	504	165	1240	2400

The four batches were weighed, ground dry for one hour, fritted and ground to pass 120 mesh. The different members in the group were made by blending the four extremes according to their combining weights.

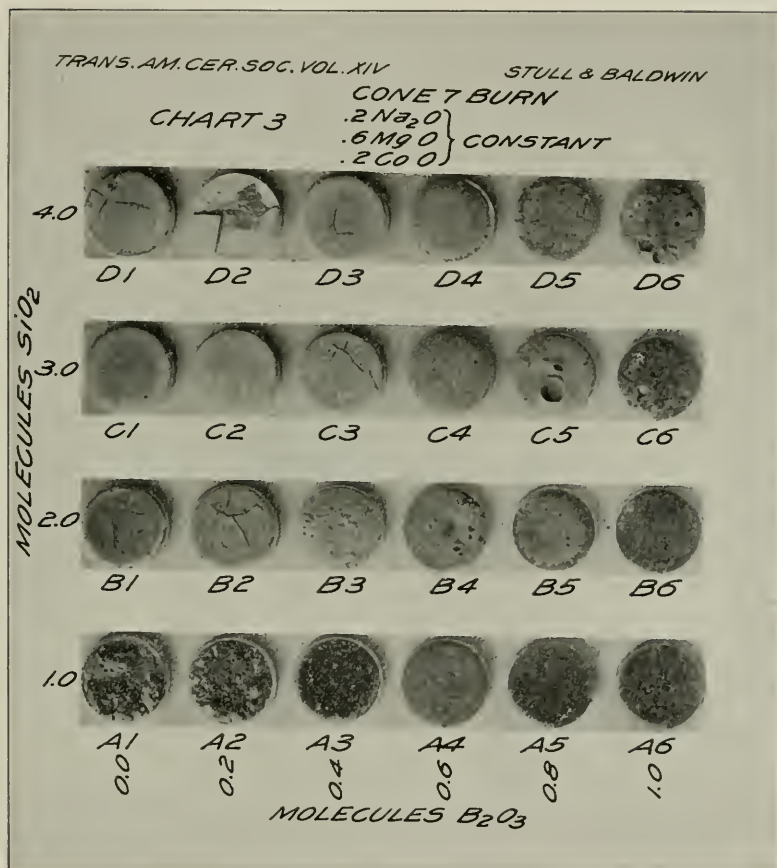
Since the glazes settled rapidly and caked, it was found necessary to employ a "colloid" in order to induce flotation for application and adhesion on drying. Glucose, dextrine and glue were tested. The best results were obtained with 4-5 per cent. glue. Such large quantities of either glucose or dextrine were required in order to produce free flotation that the glazes cracked and curled up on drying. With glue, however, a high degree of flotation was obtained, and the glazes dried without cracking.

The glazes were applied in a thick coat on 2" porcelain discs previously burned to cone 11. Three burns of this group were made, *viz.*, cones 2, 4 and 7 (Charts 1, 2 and 3). At cone 2









(Chart 1) members C 6, B 5, B 6, A 5 and A 6 were well matured. A 4 and B 4 were well vitrified, presenting pleasing matte surfaces. Refractoriness increases on a line from A 6 to D 1. Member A 6 is a deep "red-violet" in color, showing more of the red than the blue. When we pass in any direction from A 6 upward or to the left, the red diminishes and the blue increases.

At cone 4 (Chart 2) the field of matured glazes has not materially broadened. A 4 and B 4 are still matte but their surfaces have changed from an "egg shell" texture to a promiscuously interlacing needle crystal, surface.

At cone 7 (Chart 3) the matured field has broadened only a little. A 5 and A 6 have reached a high state of fluidity, have flown down over the sides of the trials and are deep blue in color with a few spots of the red-violet here and there. These glazes show that they have attacked the body vigorously. In all three burns crystallization is quite prominent and brings out the red-violet color.

The results of this group indicate that a decrease in  $\text{SiO}_2$  and an increase in  $\text{B}_2\text{O}_3$  tends toward diminishing blue and increasing red, and that 2 molecules of  $\text{SiO}_2$  as a maximum and 0.6 molecule of  $\text{B}_2\text{O}_3$  as a minimum are the approximate limits in these directions for glazes that will mature well at or below cone 7.

**Second Group.**—A second group was constructed with the idea of bringing out more of the red and less of the blue and to develop glazes maturing at lower temperatures. This group, in which the constant RO is the same as in the first group, covered the following limits:

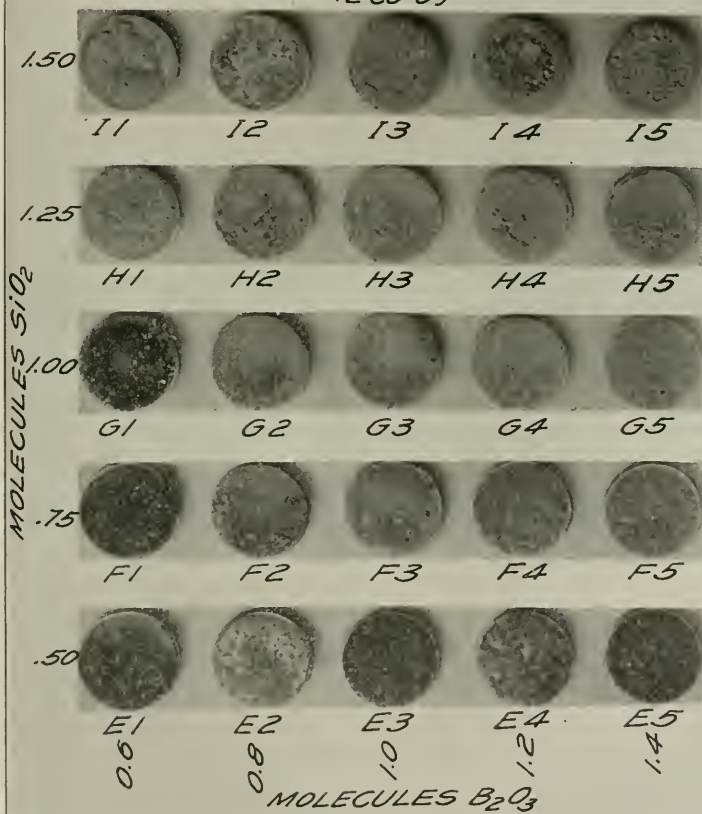
$$\left. \begin{array}{l} 0.2 \text{ Na}_2\text{O} \\ 0.6 \text{ MgO} \\ 0.2 \text{ CoO} \end{array} \right\} 0.6 \text{ to } 1.4 \text{ B}_2\text{O}_3, 0.5 \text{ to } 1.5 \text{ SiO}_2$$

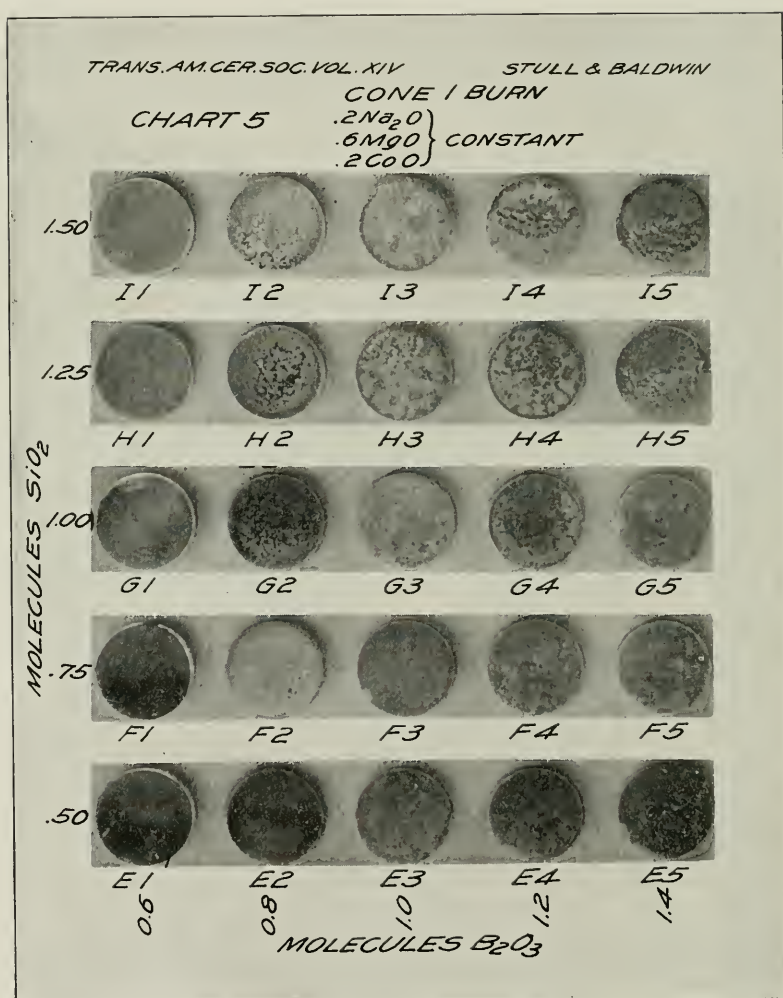
Twenty-five members were made, A 6 of the first group being stationed at the center and having the new nomenclature of G<sub>3</sub>. The members were blended from the four previously fritted extremes, the same as was done in the first group. The formulae and batch weights of the four extremes are:

TRANS. AM. CER. SOC. VOL. XIV STULL &amp; BALDWIN

CONE 02 BURN

CHART 4

 $\left. \begin{array}{l} .2 \text{ Na}_2\text{O} \\ .6 \text{ MgO} \\ .2 \text{ COO} \end{array} \right\} \text{CONSTANT}$ 




TRANS. AM. CER. SOC. VOL. XIV

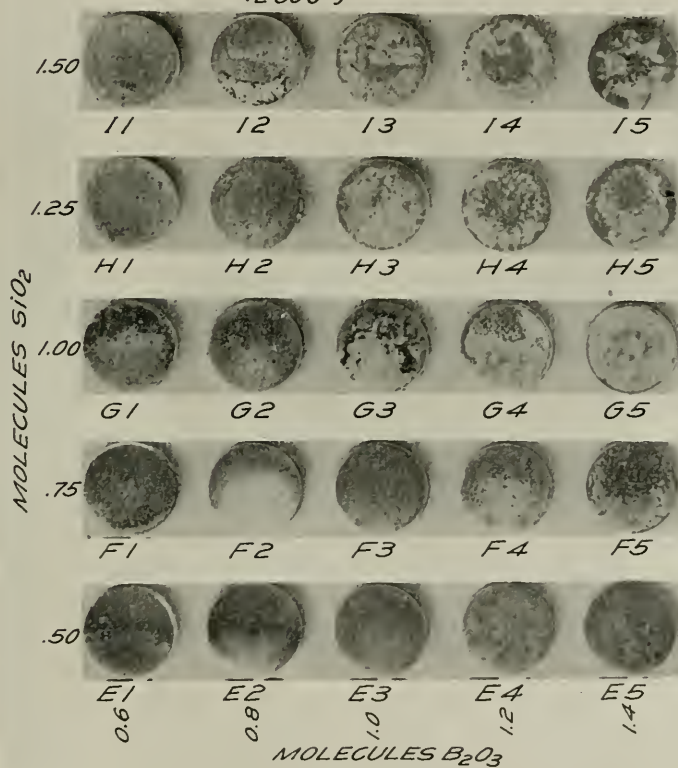
STULL &amp; BALDWIN

## CHART 6

CONE 3 BURN

.2  $\text{Na}_2\text{O}$ .6  $\text{MgO}$ .2  $\text{CoO}$ 

} CONSTANT



	Formulac					Batch weights				
	Na <sub>2</sub> O	MgO	CoO	B <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>	MgCO <sub>3</sub>	CO <sub>2</sub> O <sub>3</sub>	B <sub>2</sub> O <sub>3</sub> ·3H <sub>2</sub> O	Flint
E-1.....	0.2	0.6	0.2	0.6	0.5	212	504	165	744	300
E-5.....	0.2	0.6	0.2	1.4	0.5	212	504	165	1860	300
I-1.....	0.2	0.6	0.2	0.6	1.5	212	504	165	744	900
I-5.....	0.2	0.6	0.2	1.4	1.5	212	504	165	1860	900

Three burns were made, *viz.*, cones 02, 1 and 3 (Charts 4, 5 and 6). The red-violet color was well developed in all cases except in vertical series 1, containing 0.6 B<sub>2</sub>O<sub>3</sub>, which remained persistently matte in all three burns. Crystalline patches appear in all pieces where well matured. The red-violet color is more prominent where crystallization has taken place. Decreasing SiO<sub>2</sub> and increasing B<sub>2</sub>O<sub>3</sub> tends to throw the color toward the red and away from the blue the same as observed in the first group. Where the glazes are overfired, they have "run" considerably, attacked the body and give a clear blue. Occasionally a small group of red-violet crystals appear in a clear blue field.

Several of the glazes in this group were applied to porcelain bisque vases. In all cases where the glazes did not flow excessively or where crystallization appeared, the red-violet color was prominent. Where excessive flow took place the glaze remaining on the surface of the vase was a clear blue. In several cases where the glaze flowed down over fire clay "buttons" used as setters, the color of the glaze on these buttons was a dark green. The best glazes in the group are E 3, E 4, E 5, F 3, F 4, F 5, G 3, G 4 and G 5. Member F 4 appeared to be the best one in all three burns.

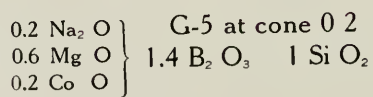
**Third Group.**—A third group was made in order to obtain lighter shades of the red-violet color. Since F 4 seemed to hold the color so persistently and showed a fair range of temperature, it was selected as the starting point. Lighter shades can be produced by blending F 4 with a similar glaze but containing no cobalt oxide. The first problem to solve was to produce such a glaze having the same heat range and fusibility as F 4. In order to save time it was decided to make a triaxial group (Chart



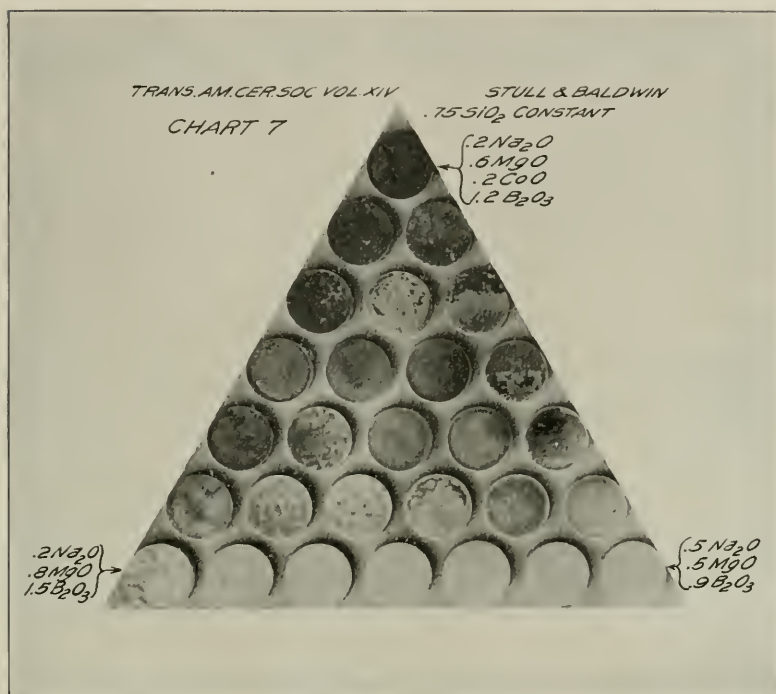




**Purple Produced by Use of Cobalt**







7) by placing F 4 at the upper apex, and the two following colorless glazes at the lower corners:



The only constant member in the group is SiO<sub>2</sub> at 0.75 molecule.

The group was made by fritting the three extremes and blending as was done in the two preceding groups. Glazes were applied to porcelain discs and burned to cone 02.

Examination of the trials indicates that there is no difference in shade or intensity of color from a content of 0.1 CoO to 0.2 CoO. The glaze near the lower left corner is a dark lavender while the one near the lower right corner is clear blue. As the MgO and B<sub>2</sub>O<sub>3</sub> decrease and Na<sub>2</sub>O increases, the color tends toward blue. Wherever crystallization appears, the red-violet or a lighter shade tending toward lavender appears.

## CONCLUSIONS.

The color violet is composed of equal intensities of red and blue. Most of the colors produced in the foregoing work lie between the violet and the red. A fusion of either soda or boric oxide and cobalt oxide gives blue. Cobalt silicate is blue. A mixture of magnesia and cobalt oxide heated to redness gives pink. The color darkens tending toward red as the temperature of calcination is increased; the color change, however, is not pronounced until very high temperatures are reached.

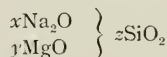
The red-violet, lavender or pink color is apparently due to some combination of magnesia with an oxide of cobalt. Decreasing  $MgO$  or increasing  $SiO_2$  causes diminishing red and increasing blue. This would indicate that the silica has broken up the magnesia-cobalt combination, thus imparting the cobalt-silica blue.

Although a fusion of  $B_2O_3$  and  $CoO$  gives blue, an increase in  $B_2O_3$  in the foregoing glazes tends toward the red and away from the blue, indicating that the magnesia-cobalt red-violet color is not only stable in the presence of  $B_2O_3$  but that the latter encourages the red by some action not definitely understood.

## DISCUSSION.

*Mr. Wilder:* I would like to ask what would be the result of increasing the heat in the trials shown on the last diagram?

*Mr. Stull:* You would tend to get less of the red-violet or lavender and more of the blue. This is probably due to the fact that the glaze becomes very fluid as the temperature increases and attacks the body vigorously. The alumina taken up changes the color to blue. We intend to continue further and try what we call an insulating glaze, by biscuiting the porcelain at 05 to 02, then applying a glaze similar to the first one on the board, as, for example:



In this glaze  $x$ ,  $y$  and  $z$  must necessarily be determined experimentally in order to fit working conditions. After applying the insulating glaze to the soft biscuit, the body is to be vitrified at cone 11 or cone 12, then the colored glaze is to be applied and

burned to maturity. In this way we hope to exclude alumina from the glaze.

*Mr. Wilder:* I would like to ask Professor Stull if he ever tried to make pigments by calcining the magnesia?

*Mr. Stull:* No, I have never done that.

*Mr. Landrum:* I made pigments by calcining iron oxide with magnesia; but I never decided whether there was a compound formed or not, nor whether there was a red-violet color from the magnesia and the ignition simply gave a more homogeneous pigment. I think there should be some trials made by igniting at a little higher temperature.

*Mr. Stull:* If the color so obtained were stable, it would work all right, but apparently these colors are very unstable during fusion in the presence of silica and alumina. It seems to me that it would be possible to make over-glaze colors along this line, if they are not fired too high and thus made too fluid. The white sample in the right-hand lower corner of the triaxial is very fusible and has attacked the body vigorously as it is pitted in places. Therefore, the over-glaze colors would have to be fired with caution, or so constituted as to possess a wide heat range.

*Mr. Will:* I make blue stains of various composition which in cone 8 and cone 10 fire turn out a pink-violet, a beautiful color, but the invariable experience has been that on being used as colors under a full glaze they turn to a deep blue. In other words, the red color is not stable except with a matte glaze. For instance, use same as a stain for a matte glaze, or a semi-matte underfired, and you get a pink glaze. From this, purple glaze is often produced by overfiring, and on firing to a gloss the same piece will show a blue color.

*Mr. Bruner:* I would like to ask a question in regard to Chart 7. Professor Stull, do you wish to give us the impression that in the lower left-hand corner, the effect was due to low soda, high magnesia, high boric acid, and that if handled correctly, these glazes will give the pink color and on the other hand with low magnesia and low boric acid, the blue color comes out?

*Mr. Stull:* That is right.

*Mr. Bruner:* Are all those pieces exposed to just about the

same heat or would you say their color was due to their position in the kiln? You do not mention anything about the fusibility and the possibility of the glazes being much more fused in one end of the kiln and the fact that when you have that condition it naturally leaves the color blue. On this piece (indicating number) you have a beautiful red-violet, as you call it, but inside it is blue. Even around the edges here you can see a little of the blue.

*Mr. Stull:* Underneath the red-violet glaze there is a thin film of blue next to the body, and where the glaze is thin the blue shows through. When crystallization takes place it brings out the red-violet color, and underfiring also brings out the characteristic red-violet color. On the inside of the piece, the thin glaze has attacked the body, thus giving the characteristic cobalt-alumina blue.

*Mr. Will:* I have applied one of these reddish blue colors to glazed Belleek ware and fired it again at glost kiln heat (cone 4-5) and there also one could not help noticing the phenomena of crystallization and the bringing out of red spots where underfired, while the balance of the piece showed a strong deep blue glaze with a high gloss.

*Mr. Burt:* I notice a number of these samples seem to show a distinct crystallization wherever the pink occurs, and I wondered whether Mr. Stull had examined it with that in mind. You get blue on the inside, but on the outer surface where you have sufficient surface glaze, you produce crystallization phenomena which develop this pink crystal. Is not the color something of a crystallization phenomenon?

*Mr. Stull:* It is true that the crystals do show the color, but the red-violet color is also developed in an underfired glaze and blue in an overfired glaze, or where the glaze is thin and has "fluxed into the body." On Chart 1, in the upper left-hand corner is the most refractory glaze in the group. It is as soft as chalk, yet it shows a light red-violet color. Alumina and cobalt together at a red heat will give a blue, while magnesia and cobalt will give pink. I do not know whether it is a chemical or a physical action that brings out the blue in one case and the pink in the other.

## INFLUENCES OF VARIABLE SILICA AND ALUMINA ON PORCELAIN GLAZES OF CONSTANT RO.

By R. T. STULL, Ceramic Laboratories, University of Illinois.

### INTRODUCTION.

Porcelain glazes of the Seger cone formula type are the most inexpensive to produce synthetically, have a comparatively wide range of maturing temperature and give but few defects. These are offered as the principal reasons for the comparative meagerness of literature pertaining to investigations on glazes of this type.

Seger<sup>1</sup> gives the following as glaze formula commonly used for porcelain:

RO, (1 to 1.25)  $\text{Al}_2\text{O}_3$ , (10 to 12)  $\text{SiO}_2$   
and for Seger porcelain<sup>2</sup>

RO, 0.5  $\text{Al}_2\text{O}_3$ , (4 to 6)  $\text{SiO}_2$

Prof. Orton<sup>3</sup> gives the following limits for characteristic porcelain glazes:

$\left. \begin{array}{l} 0.1 \text{ to } 0.5 \text{ K}_2\text{O} \\ 0.9 \text{ to } 0.5 \text{ CaO} \end{array} \right\} 0.5 \text{ to } 1.25 \text{ Al}_2\text{O}_3, 4.0 \text{ to } 12.5 \text{ SiO}_2$

### EXPERIMENTAL WORK.

In a study of porcelain glazes<sup>4</sup> of the cone formula type, two groups were made in order to illustrate the influences of variable silica and alumina. The first group covered the limits

$\left. \begin{array}{l} 0.3 \text{ K}_2\text{O} \\ 0.7 \text{ CaO} \end{array} \right\} 0.3 \text{ to } 1.0 \text{ Al}_2\text{O}_3 \left\{ 1.8 \text{ to } 7.2 \text{ SiO}_2 \right.$

and comprised eight horizontal series, from A to H, containing eighty glazes in all.

The glazes in that portion of the field covered by the A to H series were made by blending the four extremes according to their combining weights. The formulae and batch weights of these extremes are:

<sup>1</sup> Vol. II, Translations Seger, p. 705.

<sup>2</sup> Ibid., p. 706.

<sup>3</sup> Glaze lectures at Ohio State University, 1901-2

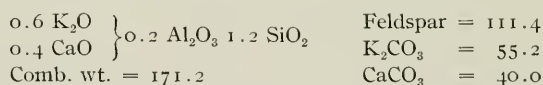
<sup>4</sup> Work done by classes 1911 and 1912, University of Illinois.

Glaze	K <sub>2</sub> O	CaO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Canadian feldspar	CaCO <sub>3</sub>	Clay		Al <sub>2</sub> (OH) <sub>6</sub>	Ohio flint
							Eng. c.c. No. 7	Tenn. b.c. No. 7		
A-1.....	0.3	0.7	0.3	1.8	167.1	70.0	..	..	...	...
A-10.....	0.3	0.7	0.3	7.2	167.1	70.0	..	..	...	324.0
H-1.....	0.3	0.7	1.0	1.8	167.1	70.0	..	..	109.2	...
H-10.....	0.3	0.7	1.0	7.2	167.1	70.0	90.3	90.3	...	240.0

Glazes in the W to Z series were also made in the same manner with the exception that it was necessary to employ a frit in order to introduce the excess K<sub>2</sub>O which could not be furnished by feldspar. The formulae and batch weights of the four extremes are:

	K <sub>2</sub> O	CaO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Frit	Feldspar	CaCO <sub>3</sub>	Al <sub>2</sub> (OH) <sub>6</sub>	Flint
W-02.....	0.3	0.7	0.25	0.6	85.6	...	50.0	23.4	...
W-6.....	0.3	0.7	0.25	4.8	21.4	125.3	65.0	...	198.0
Z-02.....	0.3	0.7	0.10	0.6	85.6	...	50.0	...	...
Z-3.....	0.3	0.7	0.10	3.0	85.6	...	50.0	...	144.0

Frit for the above:



Crazing is comparatively rare in this type of porcelain glaze, due to the vitreous nature of the body and the similarity in composition of body and glaze. In order to intensify crazing and to locate that portion of the field in which it would be most likely to occur, the glazes were applied to porous, biscuit wall tile, which shrunk considerably but were still porous at the end of the burn.

The glazes were applied a little thicker than is customary in practice, and the trials set in tile saggars and burned to cone 11 in 36 hours. The results are shown graphically in Charts I and II.

#### DISCUSSION OF RESULTS.

On Chart I, the molecular variations of silica are plotted along the abscissa and the molecular variations of alumina along

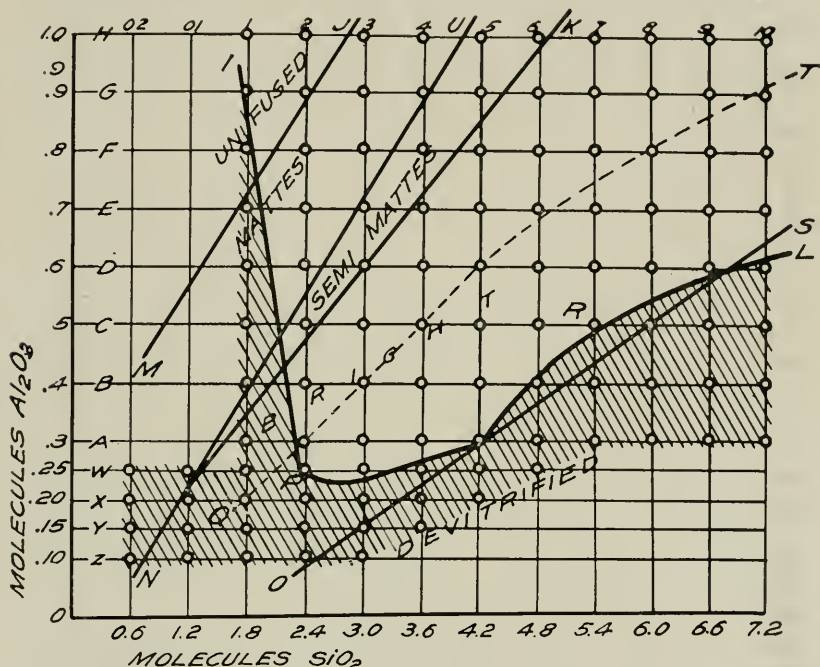


the ordinate. The letters at the left denote the horizontal series

TRANS. AM. CER. SOC. VOL. XIV

CHART I

STULL



and the numbers along the top the vertical series, so that each glaze is located by a letter and a number.

Since the RO for all glazes is constant,  $\left\{ \begin{matrix} 0.3 K_2O \\ 0.7 CaO \end{matrix} \right\}$  the formula

of any glaze can be read from the chart by referring to the ordinate for its alumina and to the abscissa for the silica. For

example, the formula of E-5 is  $\left\{ \begin{matrix} 0.3 K_2O \\ 0.7 CaO \end{matrix} \right\} 0.7 Al_2O_3 \ 4.2 SiO_2$ .

The alumina is constant in a horizontal series while the silica varies. In a vertical series the silica is constant and the alumina is the variable.

To the left of the line M J are the underfired mattes, and

between M J and N U are the matured mattes. Between N U and N K are mattes showing a sheen or slight gloss and designated as semi-mattes. The bright glazes occur between N K and O S, and below O S the glazes are devitrified. The glazes are all crazed below the line I P R L, and all sound above this line. The dotted line Q T passes through highest gloss of each series.

Beginning at the ordinate on Chart 1 and moving to the right parallel to the abscissa, it is observed that crazing and matte texture decrease with increase in silica, and that brilliancy increases up to the axis of highest gloss, Q T, beyond which brilliancy decreases, crazing increases and finally devitrification occurs.

Moving from the abscissa upward parallel to the ordinate, we see that increasing alumina has decreased crazing of glazes both high and low in silica, has decreased devitrification in high silica glazes, and increased matteness in low silica members.

A comparison of the influences of variable  $\text{Al}_2\text{O}_3$  with those of variable  $\text{B}_2\text{O}_3$  is of interest. It has been shown<sup>5</sup> that increasing  $\text{B}_2\text{O}_3$  decreases devitrification and crazing in high silica glazes and increases crazing and decreases matte texture in low silica glazes.  $\text{B}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  then function the same in high silica glazes but function oppositely in low silica glazes.

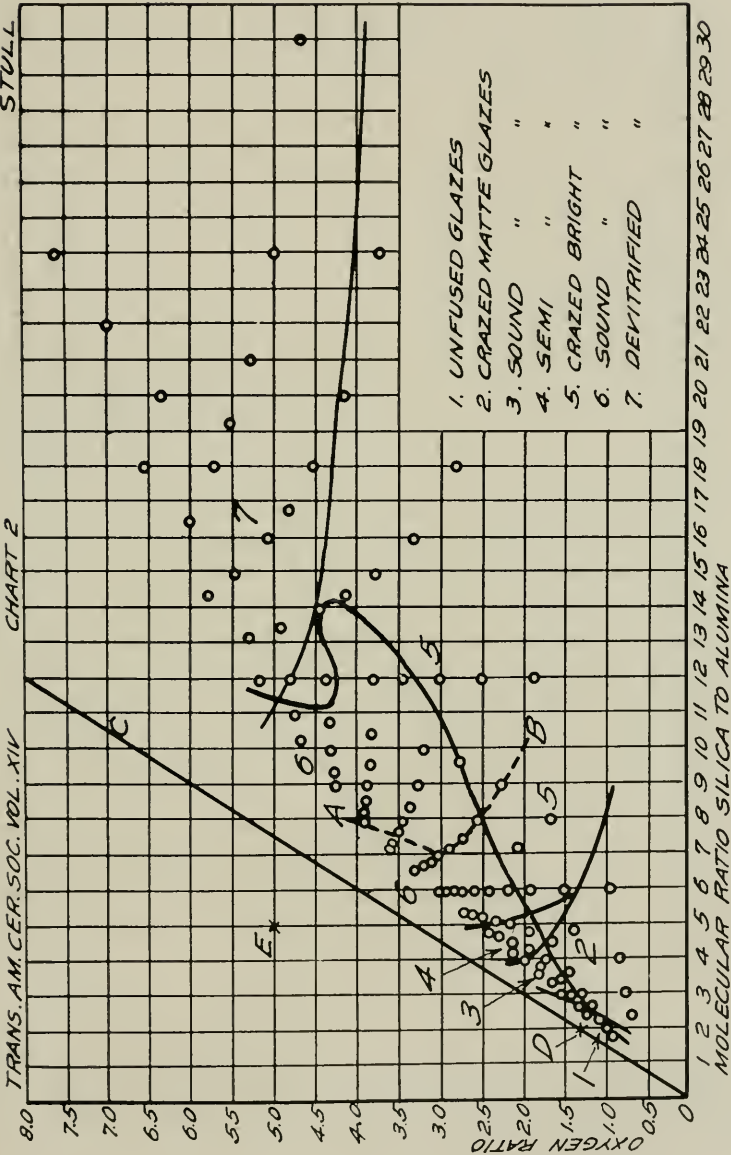
In Chart 2, the glazes are located by the molecular ratios of silica to alumina on the abscissa and by the total oxygen ratios on the ordinate. The molecular ratio of silica to alumina is independent of the total oxygen ratio, but the total oxygen ratio is partly dependent upon the silica-alumina ratio. Therefore, in plotting glaze groups similar to Chart 2, the evidence presented is influenced by one dependent and one independent variable. This must be borne in mind in drawing conclusions, otherwise they may be misleading.

The underfired mattes occur at 1, crazed mattes at 2, sound mattes at 3, semi-mattes at 4, crazed brights at 5, sound brights at 6, and glazes which are crazed and devitrified at 7. The line A B is the high gloss axis.

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<sup>5</sup> "Opalescence and the Function of  $\text{B}_2\text{O}_3$  in the Glaze," Trans. A. C. S., Vol. 12, pp. 119 to 137.





The chart shows graphically that the matte glazes fall within narrow limits and that the bright glazes occur within wide limits. In the following table is given the ratio limits within which the different kinds occur:

	O. R.	SiO <sub>2</sub> : Al <sub>2</sub> O <sub>3</sub>
1. Underfired matte glazes (at cone 11)....	0.9-1.5	1.7- 2.7
2. Crazed matte glazes (at cone 11).....	0.6-1.6	2.4- 6.0
3. Sound glazes (at cone 11).....	1.4-1.9	3.0- 4.0
4. Semi-matte glazes (at cone 11).....	1.9-2.4	4.0- 5.0
5. Crazed bright glazes (at cone 11).....	1.4-4.4	6.0-24.0
6. Sound bright glazes (at cone 11).....	2.1-4.8	5.1-13.0
7. Crazed devitrified glazes (at cone 11)....	4.5-7.6	12.0-30.0

The trials show that the best bright glazes are found between oxygen ratios of 2.5 and 3.6 and silica-alumina ratios of 7 and 8.2. The best mattes occur between O. R.'s of 1.5 and 1.8 and silica-alumina ratios of 3.2 and 3.8. The high fire matte glazes given by Prof. Binns<sup>6</sup> fall within these limits.

As the alumina increases, the positions of the glazes approach the line passing through C to the origin O. This line represents a series of glazes having constant alumina, and variable silica. The general formula which satisfies any member in this series is  $RO \propto Al_2O_3, z SiO_2$  in which  $z$  may vary from 0 to  $\infty$ . When  $z$  becomes infinitely large the formula may be reduced to the simple one of  $1 Al_2O_3, y SiO_2$ . Dehydrated kaolinite, having a total oxygen ratio of  $1.3\frac{1}{3}$  and a molecular ratio of 2, is located on the line O C at D.

The line O C is the dividing line between possible and impossible glazes. Take any point to the left of this line, as point E located by an oxygen ratio of 5 and a silica-alumina ratio of 5. From the general formula of the glaze  $1 RO, x Al_2O_3, y SiO_2$ , the following equations are obtained:

$$\frac{2y}{1 + 3x} = 5 \quad \frac{y}{x} = 5$$

in which  $x = -1$  and  $y = -5$ . The formula then of a glaze to be located at E must be  $RO, -1 Al_2O_3, -5 SiO_2$  which is impossible except mathematically. In the same manner, any

<sup>6</sup> Trans. A. C. S., Vol. VII, pp. 115-121.

other point to the left of O C may be shown to represent a glaze of the general formula  $1 \text{ RO}, x \text{ Al}_2\text{O}_3, y \text{ SiO}_2$ , in which  $x$  and  $y$  are negative.

As the dividing lines between the different glazes on Chart II approach the line O C, they curve upward, indicating that the higher the molecular content of alumina in the glaze the higher is the oxygen ratio for sound matte and bright glazes and that devitrification appears at a higher total oxygen ratio in high alumina glazes than it does in glazes lower in alumina.

The foregoing work seems to indicate that it is necessary to employ higher oxygen ratios for high alumina glazes (both bright and matte) than it is for low alumina glazes, and that the total oxygen ratio of 1 : 2 so often referred to as being best for bright glazes does not hold with, perhaps, the exception of low alumina glazes maturing at lower temperatures.

#### DISCUSSION WRITTEN AFTER READING THE ABOVE PAPER.

*Mr. Staley:* This paper is a fine example of careful and systematic work and of concise and graphic presentation of data. So well has the work been done that there is little room for discussion or comment.

From the standpoint of practical porcelain glazes, the first series, the A, B, C series, is of most interest. This may be divided into two groups of glazes: first, a group that can be made from the ordinary potter's materials, feldspar, whiting, clay and flint; and second, a group in which it is necessary to use  $\text{Al}(\text{OH})_3$ , or its equivalent. The line dividing these two groups in Chart I runs in a straight course from the glaze with 0.3  $\text{Al}_2\text{O}_3$  and 1.8  $\text{SiO}_2$  to a point that would indicate a glaze with 1.0  $\text{Al}_2\text{O}_3$  and 3.2  $\text{SiO}_2$ . It is plainly evident from the chart that the large majority of the glazes in the first group are good bright glazes at cone 11.

Inasmuch as Prof. Stull, for the sake of simplicity in blending, introduced considerable amounts of  $\text{Al}(\text{OH})_3$  into the high alumina glazes of the first group, we feel justified in predicting that if all the members of this group had been made from the materials ordinarily used by the potters, the boundaries of the matte and semi-matte areas would have been shifted somewhat toward the

upper left-hand corner of the chart. We base this prediction on the well known fact that in high alumina glazes the introduction of a given amount of alumina as the free oxide, or its equivalent, has a more decided tendency to produce matteness than the introduction of an equal amount of alumina as clay.

Professor Stull has shown beautifully the facts that under certain conditions increase of alumina can stop crazing and increase of  $\text{SiO}_2$  can cause crazing. Of course, both these statements are contrary to Seger.

The close relation between the boundary lines for crazing and devitrification in high silica glazes obviously suggests that the strains set up in the process of devitrification are responsible for the crazing. This is simply one more instance of crazing not caused by difference in coefficient of contraction

Inspection of the chart shows that a very simple rule can be devised for making a long series of good bright or matte porcelain glazes with this RO. Any raw glaze should have at least 0.05 equivalent of clay for mechanical reasons, so we will start with 0.35  $\text{Al}_2\text{O}_3$  and 2.40  $\text{SiO}_2$ . Now by adding  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  to this glaze in the proportion of 0.10 equivalent of  $\text{Al}_2\text{O}_3$  to 0.8 equivalent of  $\text{SiO}_2$ , we can make a long series of glazes lying close to the line of best bright glazes free from crazing. In terms of batch weights, this means that we can start with a glaze of the following batch: 33 feldspar, 14 whiting,  $2\frac{1}{2}$  clay and 6 flint. To this batch we add clay and flint in the proportion of 1 part clay to 1.4 parts flint. To get the longest possible series of mattes, we simply drop out the flint from the above base glaze and make successive additions of clay. The members lowest in clay of this series would be liable to craze.

*Mr. Stull:* It seems to be a question as to whether all of the glaze ingredients go into solution or not. If complete solution takes place, the difference in texture of a glaze is not so marked whether the alumina has been added as  $\text{Al}_2(\text{OH})_6$  or introduced as clay. However, a high alumina content tends to increase viscosity which operates against diffusion and consequent homogeneity.

Although these matte glazes contain some alumina introduced as the hydroxide, the trials showed that the best mattes occurred

between the O.R.'s of 1.5 and 1.8 as has been referred to. The high temperature matte glazes reported by Professor Binns in Volume VII fall within these limits. He reports his best matte as having an O. R. of 1.69. Although he used the regular potter's materials and fired at cones 8 and 9, it must be borne in mind that the replacement of clay by aluminum hydroxide and flint raises the maturing temperature. Therefore, Prof. Staley is correct in his prediction, though it is probable that the lines would have been shifted only a short distance.

The fact that increase in alumina tends to overcome crazing was, to my knowledge, first brought out by Purdy and Fox in their work on "Fritted Glazes."

A study of results plotted graphically frequently reveals far more than mere description can do. In going back to the charts, a point is observed which might be of interest to the glass manufacturer. On Chart 2 it is observed that devitrification occurs at higher oxygen ratios as the alumina increases. Since sand is the cheapest material in the glass batch, there is an advantage in using all the sand that practice will permit for common window and bottle glasses.

Frequently the manufacturer of the common grades of glass is limited in the amount of sand he can use, owing to the liability of the glass to devitrify. If alumina can be introduced or its quantity increased in the glass, a larger per cent. of sand can be employed. Not only will the alumina tend to prevent devitrification, but will also tend to counteract increased viscosity due to increased silica. The fusion temperature then would be the principal limiting factor.



## INVESTIGATIONS ON THE DIELECTRIC STRENGTH OF SOME PORCELAINS.<sup>1</sup>

By B. S. RADCLIFFE, Van Asselt, Wash.

In the following work on porcelains, four problems were investigated for the purposes of determining:

1. The relation between dielectric strength and thickness.
2. The effect upon dielectric strength due to varied heat treatment during burning and cooling.
3. The value of fire clays as raw materials for high tension insulators.
4. Influence of lime on dielectric strength.

### INFLUENCE OF THICKNESS.

The dielectric strengths of nearly all insulating materials (porcelain included) are considered proportional to the thickness. The strengths of varnished and impregnated paper insulators are exceptions. Since no experimental data was found pertaining to the relative dielectric strength to the thickness of porcelains, it was deemed advisable to make a few simple practical tests in order to determine this point for use in the work following. For this purpose, a body having the following composition, which vitrifies at cone 12, was made: Tenn. ball clay, No. 1, 15; No. Carolina kaolin, 20; Eng. china clay, 25; spar (Brandywine Summit), 20; flint (Ohio, 8 hr. grind), 20.

The body was prepared in the usual manner according to factory practice and the trials jigged in the form of small crocks (Fig. 1) which could be nested closely so that all pieces would receive the same heat treatment.

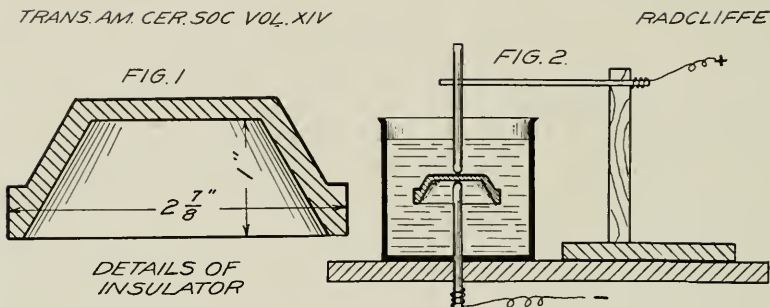
The trials were made in different thicknesses, varying from 1.4 mm. to 7 mm., by adjusting the jig tool. The trials were burned to cone 12 $\frac{1}{2}$  and punctured under transformer oil (Fig. 2), the voltage being increased gradually by a rheostat. As soon as the trial was punctured, the current was immediately broken.

The thickness at the point of puncture was measured by a micrometer. Five to ten trials made of the same thickness were punctured in each case. Whenever puncture took place

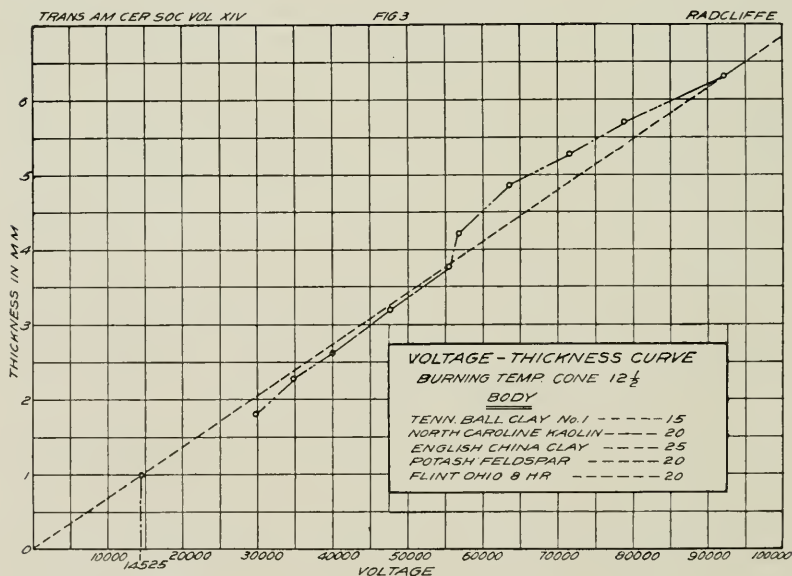
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<sup>1</sup> An abstract of work done in 1909-10 in partial fulfilment of requirements for M. S. degree in Ceramics at the University of Illinois, under supervision of R. T. Stull.





through a flaw, the trial was rejected. The voltages required for puncturing sound trials of the same thickness were averaged, the thickness being plotted on the ordinate and voltage on the abscissa (Fig. 3).



Calculating the average puncture voltage per mm. thickness for all trials tested, assuming that the puncture voltage is directly proportional to the thickness, gives a voltage of 14,525. This point is plotted and the heavy dotted straight line passes



from the origin through it. Owing to the fact that a voltage higher than 100,000 was not available, pieces over  $6\frac{1}{2}$  mm. in thickness could not be tested. However, the limits covered exceeded the requirements in the future tests.

Some interesting results were obtained by puncturing the same test piece repeatedly in the same spot. One piece, 5.7 mm. in thickness required 83,800 volts, and was given a second test and punctured at 79,000 volts, a third test required 59,300, a fourth 51,200. When the trial was shifted to a new place, the voltage required to puncture it was 77,500. Other trials were treated in the same manner giving similar results. Repeated tests through the same line of puncture weakened the dielectric strength at that point, but not until several punctures did the porcelain become too weak to resist a fairly high voltage.

Apparently the current fuses the porcelain in passing. Upon breaking several pieces through the line of puncture a glassy appearance was always noticeable.

#### INFLUENCE OF VARIABLE HEAT TREATMENT.

There seems to be no data available pertaining to the effect of rate of burning and cooling upon the dielectric strength of porcelains. In order to throw some light upon this subject, four porcelain bodies were selected from the work of Bleininger and Stull on "The Vitrification Range and Dielectric Strength of Some Porcelains." These bodies are here designated by A, B, C and D. Besides these, E was made by blending the four.

Body	Georgia kaolin	Tenn. ball No. 1	N. Car kaolin	Eng. China clay No. 7	Potash feldspar	Ohio flint
A.....	50	..	..	..	40	10
B.....	..	55	..	..	15	30
C.....	..	..	55	..	25	20
D.....	..	..	..	60	20	20
E.....	5	9	27	18	23	18

Five more bodies were made similar to these except that soda feldspar replaced the potash feldspar by theoretical molecules. These bodies are designated as A<sub>1</sub>, B<sub>1</sub>, C<sub>1</sub>, D<sub>1</sub>, and E<sub>1</sub>.

Twenty trials were made from each of the ten bodies. These

trials were divided into four sets, each set containing five trials made from each body. Each set was burned and cooled under different conditions. Set 1 was burned to cone 10 in six hours and cooled slowly in order to determine the effect of quick firing and slow cooling. Set 2 was burned to cone 13 in six hours after which air was passed through the kiln cooling the temperature down to cone 02 in one hour. The kiln was then allowed to cool slowly. Set 3 was burned to cone 10 in six hours then the temperature was gradually raised to cone 12 in an additional 14 hours, then carried rapidly to cone 17 and held for 2 hours. The kiln was then allowed to cool slowly. Set 4 was burned to cone 10 in 6 hours, gradually raised to cone 13 in an additional 18 hours and held for 20 hours. The kiln was then cooled down to cone 2 in five hours, then allowed to cool slowly.

C and C<sub>1</sub> in the first burn showed 2 per cent. porosity but all the other bodies were well vitrified.

**AVERAGE VOLTAGE PER MM. REQUIRED TO PUNCTURE TRIALS.**

Body	Part 1, Cone 10	Part 2, Cone 13	Part 3, Cone 17	Part 4, Cone 13
A.....	13260	13120	12600	13070
A <sub>1</sub> .....	12840	13100	14300	13870
B.....	13400	13000	13500	13000
B <sub>1</sub> .....	14000	13640	13620	14160
C.....	10320	13960	12760	13180
C <sub>1</sub> .....	9180	13220	13820	13860
D.....	14540	13150	13680	14100
D <sub>1</sub> .....	13400	13920	13100	13520
E.....	13550	13470	14660	12850
E <sub>1</sub> .....	13560	14820	14100	13860

The tests show that there is not a very wide difference in the dielectric strengths of the different bodies or in the manner of heat treatment. By taking the average puncture voltage per mm. for each different body for the four different burns (excluding C and C<sub>1</sub> which were porous in the first burn), we have the following table which shows that the soda feldspar bodies have higher dielectric strengths than the corresponding potash feldspar bodies in all cases except in bodies D and D<sub>1</sub> in which case D shows a higher dielectric strength than D<sub>1</sub>.

Potash spar bodies	Average voltage per mm.	Average voltage per mm.	Soda spar bodies
A	13012	13527	A-1
B	13225	13855	B-1
C	13300	13633	C-1
D	13867	13485	D-1
E	13632	14185	E-1

In order to get a comparison of the effects of variation in heat treatment, the average voltage per mm. is taken of the ten bodies for each of the four different burns. In averaging the first burn, bodies C and C<sub>1</sub> are rejected on account of their porosities. The percentage variation between maximum and minimum puncture voltages is less than 0.55 per cent. showing that the dielectric strength was substantially unaffected by the variations in burning and cooling from cone 10 to cone 17.

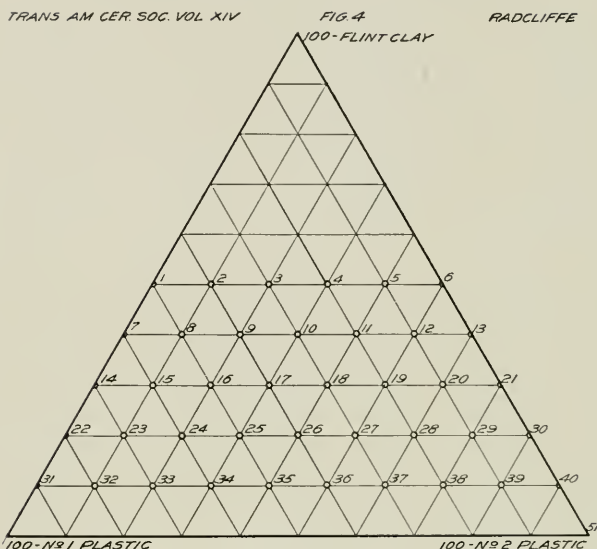
Burn	Cone	Average puncture voltage per mm.
Part I.....	10	13569
Part II.....	13	13540
Part III.....	17	13614
Part IV.....	13	13547

#### FIRE CLAYS AS RAW MATERIALS FOR HIGH TENSION INSULATORS.

The trade demands a white porcelain body for high tension insulators. Frequently a dark colored glaze (usually brown) is called for. If a colored body could be employed containing a high per cent. of fire clay, a cheaper body and a more uniform color of glaze would be the result. Insulators made from No. 2 fire clay or stoneware clay do not show a high dielectric strength. These clays vitrify at or near cone 8 while the white high tension porcelain insulators vitrify around cone 12.

In order to obtain bodies which would vitrify near cone 12, three fire clays were blended triaxially (Fig. 4). The three fire clays selected were: Olive Hill flint fire clay (calcined); Olive Hill No. 1 plastic fire clay; Bloomingdale<sup>2</sup> No. 2 plastic fire clay.

<sup>2</sup> An excellent stoneware clay, vitrifying at cone 8.



Five trials of each body were made and burned to cone  $12\frac{1}{2}$ . The porosities and puncture voltages were determined and averaged. These results are plotted on the triaxial diagram (Fig. 5), the dotted lines representing porosities and the heavy solid lines puncture voltages per millimeter thickness.

The results show that 90 parts No. 1 plastic fire clay and 10 parts calcined flint fire clay give a body of the highest dielectric strength at cone  $12\frac{1}{2}$ , and even though this body had 1 per cent. porosity, it compares very favorably with the best white porcelains in strength, 14,000 volts per mm. being required to puncture it.

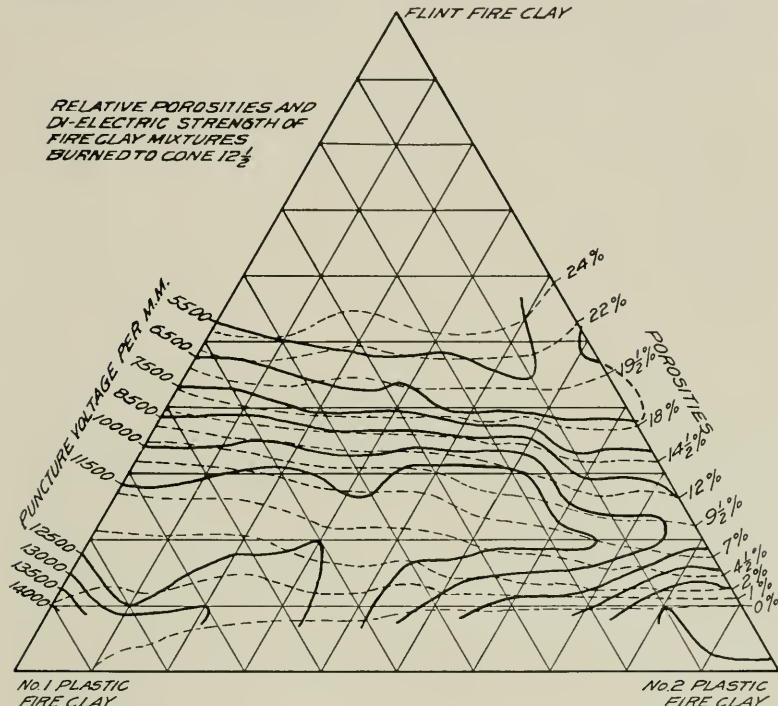
When No. 2 fire clay or stoneware clay replaces the No. 1 plastic clay, the flint clay remaining constant, the dielectric strength is lowered even though the porosity is lowered at the same time.

Bodies containing 50 per cent. or more of No. 2 clay showed evidences of a "bleb" structure, which weakened them, causing them to puncture at a low voltage. The substitution of 10 per cent. No. 2 clay for No. 1 in body 31, which gives body No. 32,

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FIG. 5  
FLINT FIRE CLAY

RADCLIFFE



did not materially lower the porosity, yet it lowered the puncture voltage from 14,000 to 12,500.

Trials which were subsequently made from bodies 14, 22 and 31 and burned to cone 14 gave a porosity for 14 of 1.34 and a puncture voltage of 13,600 per mm. The porosity of No. 22 was 0.08 and its puncture voltage 14,100 per mm. Porosity of No. 31 was zero and its puncture voltage 14,600, an increase in voltage of 600 for a decrease in porosity of 1 per cent. The white porcelain body of highest dielectric strength found in the foregoing work is the soda feldspar body E<sub>1</sub>, giving a puncture voltage of 14,820 per mm. in the part II burn. The potash feldspar body of highest dielectric strength is D, showing a puncture voltage of 14,660 in the part III burn.

In so far as dielectric strength is concerned, the foregoing

evidence indicates that vitrified bodies made from refractory fire clays stand on an equal footing with white porcelains for high tension insulators.

Good colored high tension insulators can be made from a body composed of No. 1 plastic fire clay (part of which may be calcined) and a small amount of feldspar to assist vitrification. The use of flint fire clay in the body lowers the dielectric strength by increasing porosity through its refractoriness. The plasticity, working properties and shrinkage of a fire clay body can be controlled much better than white bodies and at the same time, it would be cheaper in composition.

#### INFLUENCE OF LIME ON DIELECTRIC STRENGTH.

In order to determine the effect of lime upon the dielectric strength of porcelain, the following bodies were made in which  $\text{CaCO}_3$  was used to vitrify the bodies in place of feldspar. Part of the clay was calcined in order to control working properties. The trials were burned to cone 14 and porosities and puncture voltages determined. These results are given in the following table.

Body	Tenn. ball C. No. 1	N. Car. kaolin	Ohio flint	Calcined N. Car. kaolin	$\text{CaCO}_3$
F.....	10	45	22	23	0
F1.....	10	45	22	22	1
F2.....	10	45	22	21	2
F3.....	10	45	22	20	3
F4.....	10	45	22	19	4
F5.....	10	45	22	18	5
F6.....	10	45	22	17	6
F7.....	10	45	22	16	7
F8.....	10	45	22	15	8

The results show that 6 per cent.  $\text{CaCO}_3$  has produced a non-porous body at this temperature which does not show a high dielectric strength, and that each increase in  $\text{CaO}$  has increased the dielectric strength. F5 containing 5 per cent.  $\text{CaCO}_3$  has a porosity of 12.84 per cent. F6 shows that an increase of 1 per cent. of  $\text{CaCO}_3$  has lowered the porosity to almost zero.



Body	Per cent. porosity	Average voltage per mm.	Body	Per cent. porosity	Average voltage per mm.
F.....	28.02	..	F4.....	12.65	..
F1.....	27.60	..	F5.....	12.84	5000
F2.....	20.52	..	F6.....	0.05	6000
F3.....	17.81	..	F7.....	0.03	6700
			F8.....	0.06	8000

When the puncture tests of F6, F7 and F8 are compared to those of feldspar porcelains of the same porosities and burned at the same temperature or even a little lower, it is observed that the dielectric strengths of the feldspar porcelains are from one and one-half to twice those of the lime porcelains.

#### CONCLUSIONS.

Conclusions which may be drawn from the foregoing work indicate that:

1. For all practical purposes, the dielectric strength is proportional to the thickness of the porcelain, which is in confirmation of that assumption.

2. Rapid burning or slow burning, rapid cooling or slow cooling do not materially affect the dielectric strength of high tension insulators so long as such treatment does not develop blebs, cracks or other flaws.

3. The average of all tests made in this work showed that the molecular substitution of soda feldspar for potash feldspar in a porcelain decidedly increased the dielectric strength.

4. High-grade fire clays are capable of making high tension insulators giving as high a dielectric strength as the average potash feldspar porcelain vitrifying at the same temperature.

5. The substitution of a stoneware clay for No. 1 plastic fire clay lowers both the maturing temperature and the dielectric strength.

6. A body made vitreous by the use of lime without feldspar gives a porcelain of low dielectric strength.

#### DISCUSSION.

*Mr. Purdy:* I note that he has a series in which calcium carbonate is varied against calcined clay. An explanation of the



philosophy of a substitution of such unlike materials would be of interest.

I note also that he reports that a piece which has already been punctured will show a lower but relatively high strength when tested the second time at the same point and the same high strength when the same test piece is punctured at a new point. The only fact of value in these observations is the efficiency of oil as a non-conductor. When puncturing under oil the hole thus caused is filled with oil and not by glass as Mr. Radcliffe thinks. You can not re-test a punctured piece in the air as they did in the oil. In fact they could not have tested those shallow pieces in the air at all because of arcing around. Their data, therefore, on these two points is of value only for insulation under oil. Their conclusion should have been that their porcelain test pieces had but little, if any, better dielectric strength than did the oil they were using.

*Prof. Stull:* In order to satisfy Prof. Purdy's interest regarding the replacement of calcined clay by calcium carbonate, I will say that the calcined clay was employed merely for controlling the working properties and drying shrinkages of the bodies, as was mentioned when the paper was read. No attempt whatever was made to get a comparison of the bodies by variable lime-calcined clay. The object in view was merely to obtain vitreous bodies by using lime without resorting to additions of feldspar, and to compare the dielectric strengths of these lime bodies with those of feldspar bodies previously made.

There is no "hole" left after the porcelain has been punctured. Several of these crock shaped test pieces, after puncturing, were used as convenient receptacles for calcining small samples of kaolin at  $1000^{\circ}$  C. At this temperature the oil was completely burned off. Some of these trial pieces were broken through the line of puncture after they had served their purpose in calcining clay and these pieces showed plainly that the "hole" was filled with a glass.

Mr. Radcliffe shows that repeated puncturing through the same spot gradually weakens the dielectric strength. If puncturing leaves a hole and this hole is filled with oil, then why would

not repeated puncturing after the first give the same voltage readings for puncturing the column of oil filling the hole?

The use of the oil bath is merely to prevent arcing. If the trial pieces had been made of suitable size and shape to prevent arcing when tested in air, there is no reason why they would not have shown the same dielectric strengths in air as they did in oil.

The results are comparative whether the porcelains are tested in air or in oil. Either set of conditions would show the porcelains of highest dielectric strength.

**NOTES PREPARED AFTER READING THE PAPER.**

*Mr. Minneman:* This paper by Mr. Radcliffe is a valuable addition to our ceramic literature, for the reason that so little experimental data is available along these lines.

I think, however, that certain of his conclusions are drawn too directly from his actual results, neglecting other conditions which are bound to enter in.

In regard to the dielectric strength of soda-feldspar *versus* potash feldspar, Mr. Radcliffe says: "The soda feldspar bodies have higher dielectric strengths than the corresponding potash feldspar bodies" and "The average of all tests made in this work showed that the molecular substitution of soda feldspar for potash feldspar in a porcelain decidedly increases the dielectric strength." However, upon looking over the individual test results, it is seen that in eleven cases the corresponding soda feldspar bodies show higher dielectric strength while in the remaining eight cases the corresponding potash feldspar bodies show the higher dielectric strength. Averaging the dielectric strengths of all the soda feldspar bodies and all the potash feldspar bodies, we find the soda feldspar bodies have only about 2.5 per cent. higher dielectric strength than the corresponding potash feldspar bodies. This appears to be a decided increase in the dielectric strength, but when it is remembered that, in the method used in testing, voltage readings accurate to several per cent. are almost impossible, and variations up to 10 per cent. are quite possible, this difference of 2.5 per cent. seems almost negligible.

The voltage readings in these tests were taken, I understand, from a voltmeter placed across the low tension side of the

transformer, getting a calibration curve between the volts primary and volts secondary by means of a needle gap in the high tension side. The readings could, therefore, not be more accurate than readings from the needle gap which would be from one to four per cent., depending upon the experience of the observer. Add to this numerous uncontrollable variables, such as varying weather conditions, growth of charge in the circuit, variation in wave form and the time element in testing and it is evident that a wide divergence is quite possible.

That such a variation occurs, may be seen from the results obtained by Messrs. Bleininger and Stull, Vol. XII, Trans. A. C. S., p. 638, who made tests on the same porcelains fired at approximately the same heat treatment and tested with the same, or a very similar, apparatus. Comparing their results on the same trials and with Radcliffe's results we find variations up to 25 per cent.

Considering these points, I should say that Mr. Radcliffe's results tend to show that the dielectric strength of a porcelain is the same whether made from soda feldspar or potash feldspar so long as the porcelain is well vitrified and dense.

In regard to the use of lime, Mr. Radcliffe concludes that "a porcelain made vitreous by the use of lime without feldspar gives a porcelain of low dielectric strength."

It must be remembered that Mr. Radcliffe replaced his feldspar with lime and calcined china clay, thereby making a body of an entirely different structure. It is evident that a body made up with calcined clay and lime in place of feldspar would behave quite differently, due to the lesser distribution of the lime particles and the resulting differences in fusion, just as a body made up with equivalent amounts of sodium carbonate and calcined clay would differ from a body made up with soda feldspar. Had the clay and lime been fritted and ground until a homogeneous mixture was reached before being used in the porcelain, I think that entirely different results might have been obtained. I agree with Bleininger and Stull that dielectric strength "depends more upon sound vitrification and good mechanical structure than upon chemical composition."

Mr. Radcliffe's results do, however, show that lime used in porcelain in this way materially shortens the firing range.

The great volume of high voltage porcelain is not used under oil but in air and tests under oil often give entirely different results than do air tests. It is particularly noticeable that a porcelain not completely vitrified and having considerable absorption shows up very well when tested under oil, but breaks down much earlier when tested in air with the bottom of the test piece placed in water as is done in commercial tests.

Mr. Radcliffe mentions the puncturing of a piece under oil repeatedly in the same spot. When testing porcelain in air, after puncture once takes place there is a continuous flow of the current, and the piece ceases to act as an insulator. When testing under oil, however, this repeated puncture at a lower voltage often takes place, which leads me to believe that the oil protects the punctured spot sufficiently to give considerable insulation after the first puncture.

Consequently I should say that tests made in air, more nearly approximating conditions under which high voltage porcelain is used commercially, would be of much more practical value.

*Prof. Stull:* The question of experimental errors enters into all research work of this character. In theory, however, there is such a thing as absolute accuracy. The value of research work depends largely upon the accuracy in executing the work and the extent to which experimental errors are avoided or eliminated.

One of the greatest sources of error which Mr. Minneman failed to mention is due to variations in structure of different pieces made from the same body. It is impossible to eliminate minute air bubbles and to mould two pieces of porcelain so that they will have identically the same structure.

Where it is impossible to eliminate experimental errors or to deduct such errors by calculations from known data, it is customary to make several tests and to consider the mean average as a means of reducing such errors to a minimum.

As has been mentioned, Mr. Radcliffe made from five to ten different puncture tests for each different body under each different set of conditions, excluding all trials in which flaws due to

moulding were apparent and taking the mean average of apparently sound pieces.

Mr. Minneman states that "it is seen that in eleven cases the corresponding soda feldspar bodies show higher dielectric strength while in the remaining eight cases the corresponding potash feldspar bodies show higher dielectric strength."

It was stated in Mr. Radcliffe's paper when read that "bodies C and C<sub>1</sub> are rejected on account of their porosities" (in the first burn). Since these two bodies are porous they are not at all comparable with the others which were well vitrified, hence, it is legitimate and proper to exclude them from the calculations. Excluding C and C<sub>1</sub> in the first burn, it is observed that the comparison is as twelve to seven, as Mr. Minneman has evidently made an error in count.

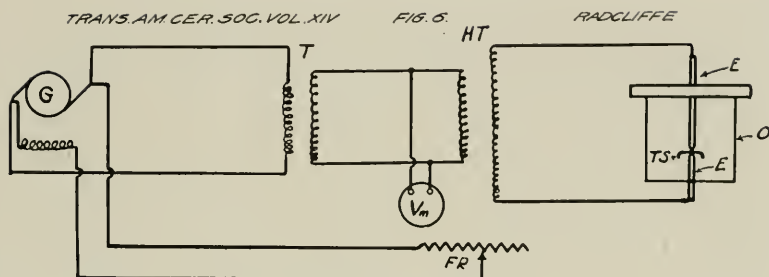
Since five trials of each porcelain for each of the four burns were tested, the average puncture voltage per mm. (excluding C and C<sub>1</sub> in the first burn) is calculated on ninety-five trials punctured for each type of porcelain. Taking the average of such a large number of tests tends to give an accurate comparison.

The physical properties of ceramic mixtures depend upon composition and method of treatment. The treatment of the potash feldspar porcelains and the corresponding soda feldspar ones were carried out as nearly alike as possible. Since the two different kinds of feldspars are bound to exert some differences upon the physical properties, and one of these physical properties is "dielectric strength," it is more logical to conclude that the substitution of soda feldspar for potash feldspar has increased the dielectric strength since this conclusion is backed by the average results of ninety-five puncture tests of each of the two types of porcelain.

*Mr. T. H. Armine:* The puncture tests made upon the porcelains referred to in Mr. Radcliffe's paper were made under my supervision in the Engineering Experiment Station at the University of Illinois.

The accompanying sketch shows the connections used in





the test: G is a generator of 60 kilowatts capacity which produces practically a sine wave of electromotive force. T is a transformer stepping the voltage of the generator up by a four to one ratio. HT is a transformer of 10 kilowatts capacity which is designed to step from 440 up to 100,000 volts. FR is the field rheostat of the generator by means of which the high tension voltage was varied. O is a stoneware jar having a brass electrode, E, inserted through a hole in its bottom. A similar electrode, E<sup>1</sup>, was arranged in such a manner that it was brought in the same straight line as E and so that it could be pulled up away from E to permit of putting the porcelain sample TS between the electrodes.

The first procedure was to obtain a calibration curve of the apparatus. The connection was removed from the electrode E and E<sup>1</sup> and a needle gap was placed across the high tension side of the transformer. With various settings of the needle gap the voltage was gradually brought up by varying FR until the discharge took place across the gap, at which time the voltage on the low tension side of the transformer was read by means of the voltmeter V<sub>m</sub>. In this way the relation between "volts primary" and "length of the needle gap" was obtained. Then by means of the well known A. I. E. E. curve between "distance between needle points in air" and "volts," the "centimeters width of needle gap" were translated into "volts secondary." This calibration was repeated several times and good checks were obtained so the average curve between "volts primary" and "volts secondary" was adopted as the calibration curve.

In making the puncture tests the connection was made as shown in the diagram, a porcelain test piece, TS, was placed between the electrodes and the stoneware jar O filled with transformer oil. The voltage was gradually brought up by varying FR until puncture took place, at which time the "volts primary" were read by means of the voltmeter Vm. By means of the calibration the curve "volt secondary," that is, the volts to produce rupture, could be obtained. In all the tests care was taken that the rate of increase in voltage was uniform for all samples.

In Mr. Minneman's discussion of this paper the question of accuracy of the results obtained is brought up. Since the calibration curve was obtained by reference to a needle gap it may be in error by as much as 4 per cent. Since it was made all in one day under as constant conditions of weather, etc., as possible and since several checks were made it is probable that the error in calibration is less than this. However great the error in the calibration curve is, it is a constant error and affects the reading only when considered as absolute values of voltage and does not affect the relative values obtained for the various samples. For instance, the tests upon soda feldspar *vs.* potash feldspar involve none of "the uncontrollable variables such as varying weather conditions, growth of charge, variation of wave form and time element," mentioned by Mr. Minneman. The values obtained for these two porcelains should be closely comparable even if the absolute values of voltage were seriously in error since the errors should be the same for both sets of tests.

Mr. Minneman also mentions that "when testing a porcelain in air, after puncture takes place there is a continuous flow of current and the piece ceases to act as an insulator." This same action takes place with tests under oil. At the instant of rupture the current follows the arc and continues to follow it as long as the voltage is on in the same way as it does with a test in air. A second application of voltage in the same spot does show that there is still considerable dielectric strength after the first puncture. This dielectric strength is not, however, due to the protective effect of the oil. The current which follows the arc fuses the porcelain and when the circuit is broken the fused porce-



lain solidifies in place, forming a glassy spot. Due, perhaps, to flaws and to the presence of foreign material such as carbonized oil, which probably prevents the formation of a homogeneous structure, the strength on second puncture is less than on the first. The voltage at which a sample will puncture the second time has, I believe, no relation to the real dielectric strength, *i. e.*, on first puncture, of the porcelain sample. I believe that the only serious effect of testing under oil would be with very poorly vitrified porcelains such as are obviously not fit for high tension insulators. In testing these porous porcelains comparable results possibly would not be obtained under oil.



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## BULLETIN No. 17

### DEPARTMENT OF CERAMICS

A. V. BLEININGER, Director

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## THE EFFECT OF ACIDS AND ALKALIES UPON CLAY IN THE PLASTIC STATE

BY

A. V. BLEININGER AND C. E. FULTON

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## NOTE ON THE DISSOCIATION OF CALCIUM HYDRATE

BY

R. K. HURSH

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## NOTE ON THE RELATION BETWEEN PREHEAT- ING TEMPERATURE AND VOLUME SHRINKAGE

BY

R. K. HURSH

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## THE EFFECT OF ACIDS AND ALKALIES UPON CLAY IN THE PLASTIC STATE.

A. V. BLEININGER AND C. E. FULTON, Urbana, Ill.

### INTRODUCTION.

The effect of acids, alkalies and salts upon clay suspensions (slips) has been discussed frequently, and the work of Simonis, Mellor, Rieke, Boettcher, Ashley, Foerster and Bollenbach deals with the viscosity and other phenomena of systems in this state. But little is known concerning the effect of such reagents upon clays in the plastic condition which differs from that of a suspension, due to the cohesive influence of the particles upon each other.

It has been realized for some time that the properties of clays in the wet state are influenced by the presence of alkalies and acids. Seger explains the increase in the plasticity of clay upon storing by the assumption that the fermentation of organic substances results in acids which neutralize the alkalinity due to the decomposed feldspar, and in addition bring about the "sour" condition which accompanies the improvement in working qualities. Rohland<sup>1</sup> discusses this subject from the theoretical standpoint and makes quite definite statements with reference to the principles underlying the effect of various reagents upon clays in the plastic state. He arrives at the conclusion that the plasticity of clays is increased by the presence of  $H^+$  ions, while, on the other hand, the  $OH'$  ions are active in the opposite direction. According to Rohland, the plasticity is likewise increased by the addition of colloids like tannin, dextrine, etc., as has been shown by the work of Acheson, fine grinding and the storage of the clay in cool and moist places. It is supposed that the increase in plasticity is coincident with the coagulation which is primarily due to the presence of the hydrogen ions; it is retarded by the hydroxyl ions. The salts of strong bases and weak acids which dissociate  $OH'$  ions hydrolytically produce an effect similar to that of the hydroxyl ions. Neutral salts, Rohland goes on to say, with but few exceptions, are indifferent in their

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<sup>1</sup> "Die Tone," pp. 35-19.

effect, though some appear to show a contradictory behavior, which has not yet been explained. "The effect of the hydroxyl ions may be weakened, compensated or strengthened by the action of the salt in question. Thus borax is an example of the first class and sodium carbonate of the second."

The same writer further says that with some clays the addition of  $\text{Na}_2\text{CO}_3$  brings about an improvement in plasticity, while ordinarily the same reagent behaves in the opposite sense, due to the hydrolytic dissociation of  $\text{OH}'$  ions. It is possible that the effect of hydroxyl ions might be neutralized by the  $\text{CO}_3''$  ions.

#### DRYING SHRINKAGE.

A decided lack of data exists with reference to the determination of the effect of reagents upon the plasticity of clays. It was thought advisable for this reason to begin work along this line without reference to any theoretical speculations. The most obvious criterion to be used in this connection is the drying shrinkage, which, from what we know of the properties of clays, is a function of plasticity. It is evident that any effect caused by the addition of reagents will at once be indicated by the shrinkage of the clay.

In this series of experiments Georgia kaolin was used. This clay was found to show an acid reaction when tested with phenolphthalein. This would indicate that the addition of acid should bring about no decided change in the clay, a fact which was verified by experiment. The reagents employed were  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{NaOH}$  and  $\text{Na}_2\text{CO}_3$ . In carrying out the work a thoroughly mixed sample was first prepared so that variations due to differences in composition were reduced to a minimum. The test specimens were in the shape of bars  $3\frac{5}{16} \times 1 \times \frac{5}{8}$  inches. Even the most careful linear shrinkage measurements by means of the vernier caliper were found to be unsuitable for the work. A volumometer permitting of readings to 0.05 cc. was then employed. The measuring liquid used was petroleum from which the lighter oils had been expelled by heating. The bars were at once weighed and allowed to dry at the laboratory temperature for three days, after which they were heated at  $110^\circ$  to constant

weight, and their shrinkage determined. For each concentration of reagent three bars were made and measured.

**Clay and Water.**—A study was first made of the drying shrinkage of the clay with different amounts of water, ranging from the soft state in which the clay could be barely molded to the condition of minimum water content when molding was likewise difficult for the opposite reason. The shrinkage relations to the various contents of water are shown in Fig. 1. The third point on the curve, showing a shrinkage of 10.45 per cent. with a water content of 32.8 per cent., represents the most workable state. Any increase in water above this point is at once observed by the rapid softening of the mass. The clay hence is well suited for the work at hand, owing to the ease with which the condition of best working behavior is recognized in distinction from many other plastic clays which possess a long working range.

**Effect of Acid.**—Upon adding from 0.025 to 0.525 gram of hydrochloric acid to 100 grams of clay, we observe from Fig. 2 that the shrinkage is not materially affected by this reagent. While two maxima of somewhat greater contraction are noted, the principal result seems to be a reduction in shrinkage, contrary to what might be expected from Rohland's statements. The fact remains, however, that conditions are more complex than they seem, due to the probable solution of various salts in the clay as well as the formation of some chlorides by the acid.

It was thought that further insight into the effect of the acid might be obtained by calculating the total and the shrinkage water in terms of the true clay volume, *i. e.*, weight divided by the density of the powdered substance, according to the relation:

$$\frac{100(v_1 - v_2)}{\frac{w}{d}} = \text{per cent. (by volume) shrinkage water.}$$

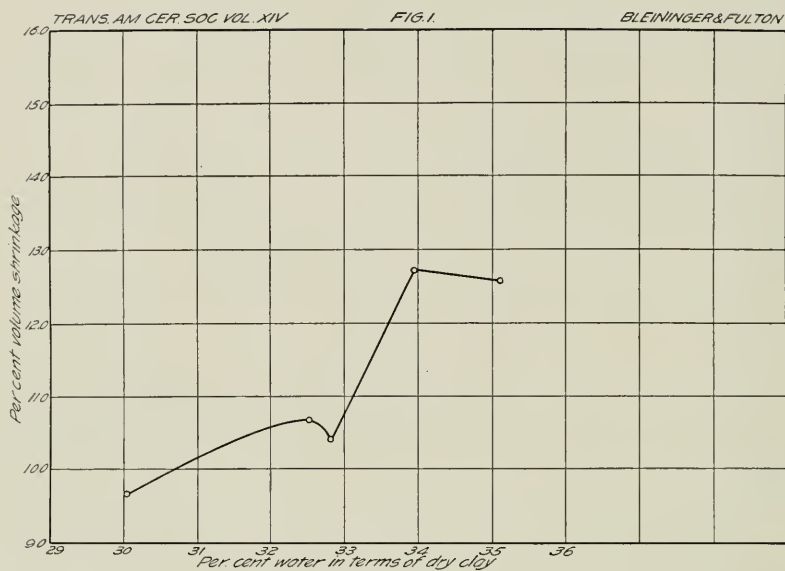
Where  $v_1$  = volume of wet brickette,

$v_2$  = volume of dry brickette,

$w$  = weight of brickette, dried at 110° C.,

$d$  = density of the dry and powdered clay.





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FIG. 3

BLEININGER &amp; FULTON

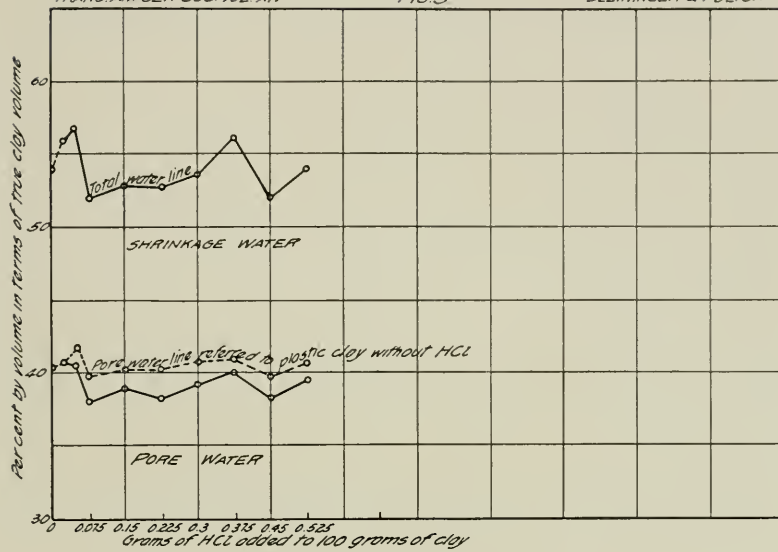
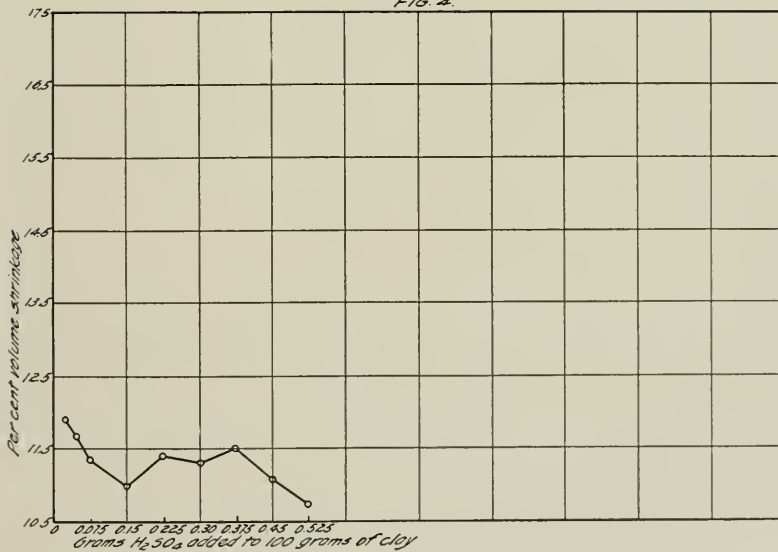
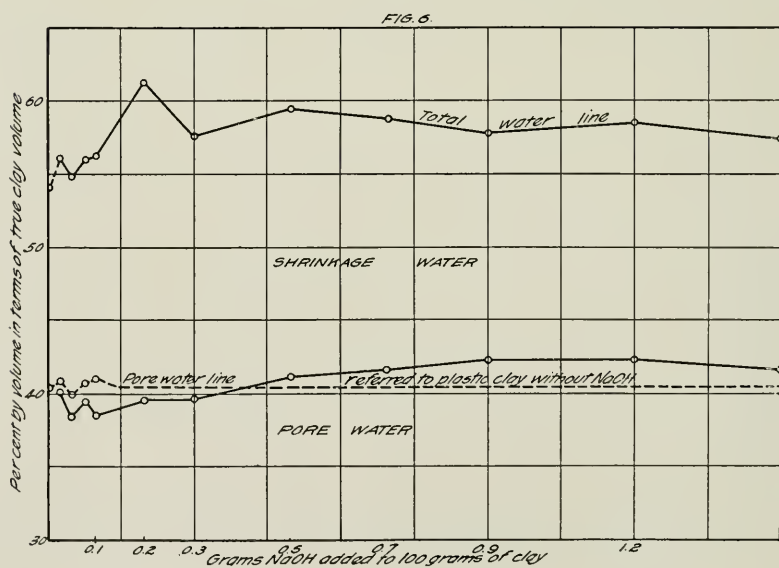
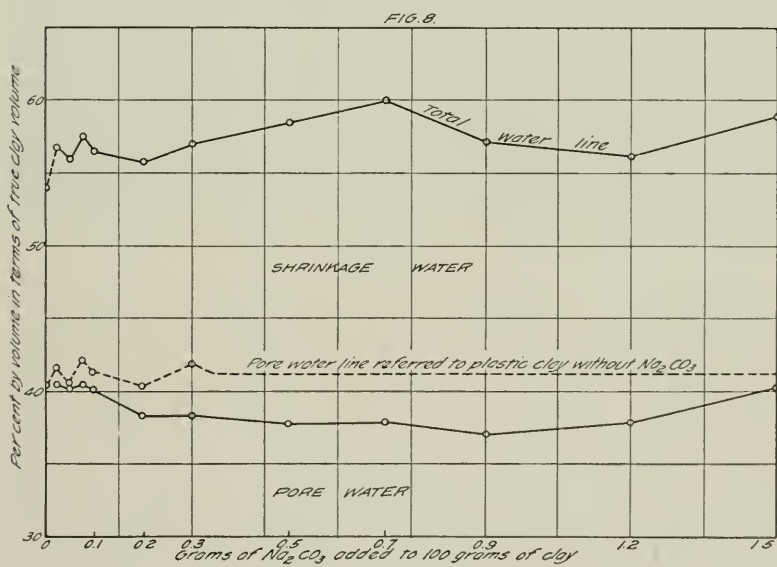
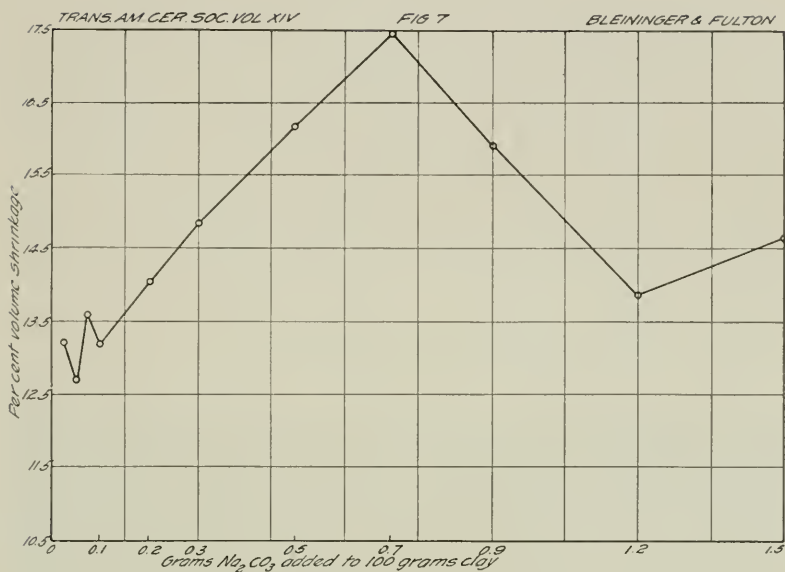


FIG. 4.







Similarly, the volume of the total water in terms of the true clay volume is calculated.

In the diagram of Fig. 3, the respective volumes of total and shrinkage water are shown. The boundary between the volumes of water and that of clay is, of course, the line representing zero water and 100 volume per cent. of clay. It is shown in Fig. 3 that the content of pore water has been decreased, that of the shrinkage water having been increased both at the expense of the pore water and due to the rise in the total water content at the two max. points.

The addition of sulphuric acid likewise tends to decrease the shrinkage as is shown in the diagram of Fig. 4.

**Effect of Alkalies.**—The influence of NaOH is illustrated in the diagram of Fig. 5. It is at once noted that with 0.2 per cent. of this reagent a striking max. point is reached, indicating a marked increase in shrinkage, contrary to what we should expect according to Rohland's views. Only after adding larger amounts does the contraction descend towards the normal value. Here again, according to Fig. 6, the increased shrinkage is due in part to the specific effect of the reagent in increasing the distance between the particles in the plastic state and, in part, to the denser structure of the clay upon drying. Beyond the max. point this condition changes, since the pore water line rises above the normal level. Since, at the same time, the total water line descends, the shrinkage is gradually decreased. The structure of the dried clay is thus more open with the higher contents of NaOH than with the smaller additions.

The growth in shrinkage is still more pronounced in the case of  $\text{Na}_2\text{CO}_3$ , Fig. 7, a phenomenon contrary again to Rohland's statements, although, of course, in this case the effect of the  $\text{CO}_3$  ion might have proven a factor, especially if absorption has taken place to any appreciable extent. However, even under this assumption, it is somewhat improbable that the carbonic acid could have brought about such a change where other acids failed to accomplish anything like the same result. In this diagram the maximum occurs with 0.7 per cent. of the reagent. With larger concentrations the shrinkage is again reduced, but appears to gain once more with amounts beyond 1.2 per cent.

As may be observed from the diagram of Fig. 8, the pore water volume is diminished throughout this series with a gradually increasing total water content up to the maximum.

#### DEFLOCCULATION SERIES.

It was thought desirable to study the effect of the acids and alkalies upon the clays as regards deflocculation, using solutions of the same concentration present in the plastic clay, as shown by the preceding curves. To illustrate: If to 100 grams of clay, requiring 34.9 per cent. of water, 0.025 gram  $\text{Na}_2\text{CO}_3$  was added, this would represent a solution carrying  $0.025 \div 34.9 = 0.000716$  gram  $\text{Na}_2\text{CO}_3$  per cubic centimeter of water. Such solutions

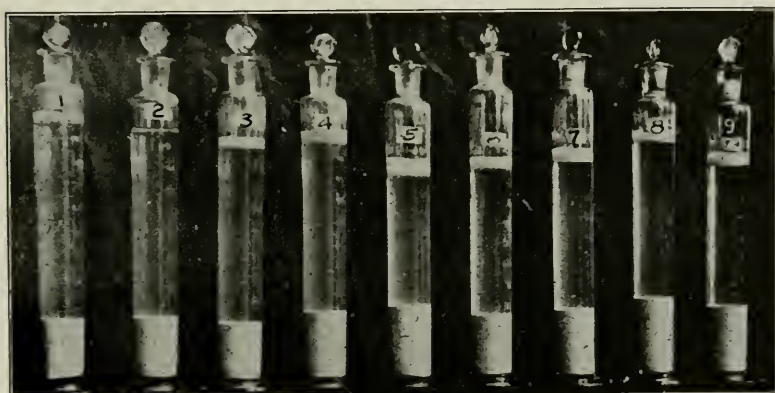


Fig. 9.

No.	Wt. clay. Grams	Wt. $\text{Na}_2\text{CO}_3$ , Grams	Water, cc.	Volume of sediment, cc.	Condition of turbidity of supernatant liquid
0	5	...	98	18.0	Clear
1	5	0.0713	98	19.5	"
2	5	0.1423	98	21.8	"
3	5	0.2296	98	24.3	"
4	5	0.4529	98	28.0	"
5	5	0.6803	98	27.4	"
6	5	0.8913	98	28.0	"
7	5	1.0659	98	28.0	"
8	5	1.3549	98	28.0	"
9	5	1.5511	98	28.0	"

were made up of concentrations corresponding to the various points in the preceding curves. In each case to 5 grams of clay 98 cc. of the solution were added in a graduated tube. The tubes were placed in a shaking machine for 90 minutes and allowed to stand. It was found that the clay itself, without any reagent, settled well, showing a clear, supernatant liquid and a sediment occupying 18 cc.

It was shown that the addition of acid produced no change, excepting in the volume of the sediment, which was finally increased from 18 to 28 cc., as is observed from Fig. 9.

The sodium carbonate solutions, on the other hand, started with conditions of complete deflocculation (Fig. 10). The sediment volumes are shown in the table accompanying each figure.

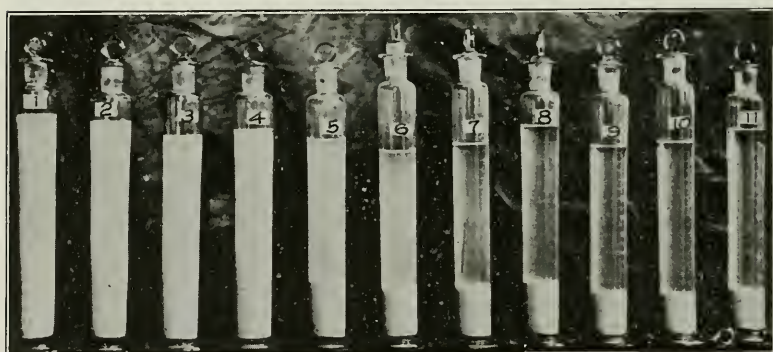


Fig. 10.

No.	Wt. clay, grams	Wt. $\text{Na}_2\text{CO}_3$ , grams	Water, cc.	Volume of sediment, cc.	Condition of turbidity of supernatant liquid
0.....	5	..	98	18	Clear
1.....	5	0.0702	98	4.5	Very turbid
2.....	5	0.1426	98	19	Very turbid
3.....	5	0.2090	98	24	Slightly less turbid
4.....	5	0.2822	98	24	Less turbid
5.....	5	0.5713	98	20	Slightly turbid
6.....	5	0.8388	98	20	Slightly turbid
7.....	5	1.3642	98	21	Almost clear
8.....	5	1.8571	98	19	Clear
9.....	5	2.5059	98	18	Clear
10.....	5	3.4006	98	18	Clear
11.....	5	4.0709	98	18	Clear



The maximum point of the shrinkage curve corresponds to tube No. 8, where the supernatant liquid is clear for the first time.

#### CONCLUSIONS.

The writers do not attempt at this time to explain the phenomena on theoretical grounds. It is evident that the conditions are quite complex and in order to explain them still further modes of attack must be sought for. The rules laid down by Rohland do not seem to apply, since in the main the acids clearly caused shrinkage to decrease while the alkalies produced the reverse effect, which is contrary to his statements. In order to be fair, however, attention must be called to the fact that shrinkage in this work has been considered a measure of plasticity, while Rohland speaks of plasticity itself without attempting to correlate this property with any numerical value. As is well known, there is at the present time no clear conception as to the relation between plasticity and shrinkage excepting the general fact that the plastic clays as a class show a greater drying shrinkage than the leaner ones.

#### DISCUSSION.

*Mr. R. J. Montgomery:* I should like to ask Prof. Bleininger how long those slips in the cylinders had stood when the photographs were taken.

*Prof. Bleininger:* Twenty-four hours. I might add also that in making the volume determinations they were stored twelve hours in a moist chamber in order to bring about some sort of an equilibrium between the clay and the reagent.

*Mr. Kerr:* I should like to raise the question as to what determinations, if any, were made of the electrolytes present in the clay before the acids and alkalies were added. Was any general data obtained upon this point?

*Prof. Bleininger:* No direct determination was, of course, made. However, you have seen the series of tubes which ought to indicate pretty clearly to one familiar with this work whether the initial conditions are acid or alkaline. We are principally endeavoring to get at the experimental facts without much regard to theoretical assumptions. The evidence so far obtained along these lines is not sufficient to base upon it any definite

line of procedure. The work of Veimarn especially has disturbed previous conclusions by his very startling claims with reference to colloids. We thought it wise to work along the lines which I have indicated.

*Mr. Kerr:* The only point which I wished to bring up was that if one clay contained positive ions in excess and another clay negative, the addition of either acid or alkali to one clay would not correspond to a similar addition to the other clay. Some clays give a strongly acid reaction, others a weakly acid, while still others are somewhat alkaline. Data upon neutralization might be included.

*Prof. Bleininger:* This is brought out in the deflocculation experiments. At the same time corrections work very well in theory, but when you come to make them you will find that neutralization does not necessarily follow. I, of course, want to check Mr. Ashley's work in this investigation in a general way. I realize we have learned a good deal from his work and I want to say that he is to be given great credit for having started work of this kind.

*Mr. Purdy:* I would like to ask if any experiment has been made to determine whether, as a rule, trivalent electrolytes coagulate clays more readily than do the uni- and divalent salts.

*Prof. Bleininger:* I would say that it has been done with various materials.

*Mr. Purdy:* Has it been done with clays? I would like to see some experiments tried on that and reported, because I have been unable to show that the trivalent salts have any more effect than the other. That is one of the respects in which the clay is different.

*Prof. Bleininger:* Mr. Ashley, of course, has done such work.

*Mr. Purdy:* That is what he did not do, he accused himself on that point.

*Prof. Bleininger:* I think he did work with phosphates. Of course, as I said before, this work is being continued and we expect to take representative reagents.

*Mr. Kerr:* What measurements other than volume shrinkage were made?

*Prof. Bleininger:* We hope to take up various things in

time. One of them is a vapor tension investigation, for which a special apparatus is now being designed.

*Prof. Grout:* I would like to ask if the curves which are drawn there, such as the first curve which you show on the screen, were the average of a series of results on one clay or just one series of tests.

*Prof. Bleininger:* Taken as the average of three determinations in each case.

*Prof. Grout:* I wondered if that approximation of a maximum was so characteristic that you could report it for publication on one series of tests; whether your area of determination was not such that you might not safely report it.

*Prof. Bleininger:* Well, we were able to get very good checks, also we notice that the two acids are behaving very similarly. We recognize, however, that there are a good many factors involved which it is almost impossible to correlate in a technical investigation of this kind. Of course, if we were to carry on this investigation from a strictly physical chemical standpoint, we would proceed along somewhat different lines.

*Mr. Potts:* I would like to ask Prof. Bleininger just what practical application he expects to make of that treatment. Does he propose to make kaolins plastic?

*Prof. Bleininger:* I haven't any idea as to what this information could be used for and am indifferent in regard to that point.



## NOTE ON THE DISSOCIATION OF CALCIUM HYDRATE.

By R. K. HURSH.

### INTRODUCTION.

The present study, which was intended to be of a technological rather than of physical-chemical nature, was undertaken with the purpose of learning more regarding the properties and behavior of the compound  $\text{Ca}(\text{OH})_2$ . The work has a practical bearing in demonstrating the value of methods of thermal study upon problems dealing with the dehydration of limes, cements and plasters.

A number of values have been given for the dissociation temperature of calcium hydrate. Herzfeld<sup>1</sup> says that dissociation evidently begins at  $470^\circ$  to  $500^\circ$  C. He gives the thermal effect of slaking  $\text{CaO}$  as 1.51 cal. per gram of  $\text{Ca}(\text{OH})_2$  and the maximum temperature of formation as  $468^\circ$ . H. Rose<sup>2</sup> found that pure calcium hydrate lost nothing at  $100^\circ$  C., absorbed  $\text{CO}_2$  at  $200^\circ$  and  $300^\circ$ , and began to lose  $\text{H}_2\text{O}$  at about  $400^\circ$  C.

Le Chatelier<sup>3</sup> gives a vapor tension of 100 mm. at  $350^\circ$  C., and 760 mm. at  $450^\circ$  C.

Tichborne<sup>4</sup> found the precipitate from a heated solution of lime water to show a loss on blasting that corresponded to the formula  $3\text{CaO} \cdot 2\text{H}_2\text{O}$ . Others using similar methods failed to find such a hydrate.

Dr. Johnston,<sup>5</sup> whose work is taken up further on, found the dissociation pressure of  $\text{Ca}(\text{OH})_2$  to reach 760 mm. at  $547^\circ$  C.

### METHODS AVAILABLE.

There are several methods of studying the dissociation of hydrates, such as the making use of heating curves, the determination of the aqueous pressure in direct or differential tensimeters, and the method depending upon the determination of the loss of weight at different temperatures

<sup>1</sup> Handbuch der anorg. Chem., C. Dammer.

<sup>2</sup> Pogg. Ann. du Physik u. Chem., LXXXVI, 105.

<sup>3</sup> Handbuch der anorg. Chem., 22, Gmelin-Kraut.

<sup>4</sup> Chemical News, XXIV, 199.

<sup>5</sup> Ztschr. phys. Chem., LXII, 330.

**HEATING CURVE METHOD.**

A portion of the substance is placed in a furnace with a thermocouple touching it and another near it. The furnace is heated, and the temperatures of the furnace and substance are noted. At the point where dissociation takes place, a lag may be noted in the heating curve due to the endothermic reaction, *i. e.*, the absorption of heat due to the expulsion of water. It is frequently difficult and sometimes impossible to determine the point by this means, owing to the small amount of heat required for the reaction of the slow rate of dissociation. Distinction may be made between mechanically held or dissolved water and chemically combined water. In the case of chemical water, the lag will occur abruptly at the temperature of dissociation. Mechanical or dissolved water will pass off gradually over a range of temperature, and the lag due to these is gradual, showing no abrupt break at a definite temperature.

In the use of heating curves, close regulation of the temperature is very necessary to get reliable results. There should be no fluctuations in the heating of the furnace. Three general methods may be followed in the heating:

Indiscriminate, in which no attention is given to the rate of the furnace curve, and only the lags in the heating curve of the substance are given attention.

Constant rate, in which the temperature of the furnace is raised at a uniform rate.

Constant difference, in which a uniform difference between furnace temperature and that of the material is maintained. This method is the best, although the most difficult one of the three. The constant rate method gives good points, but the lag will, in most cases, be sloped instead of horizontal.

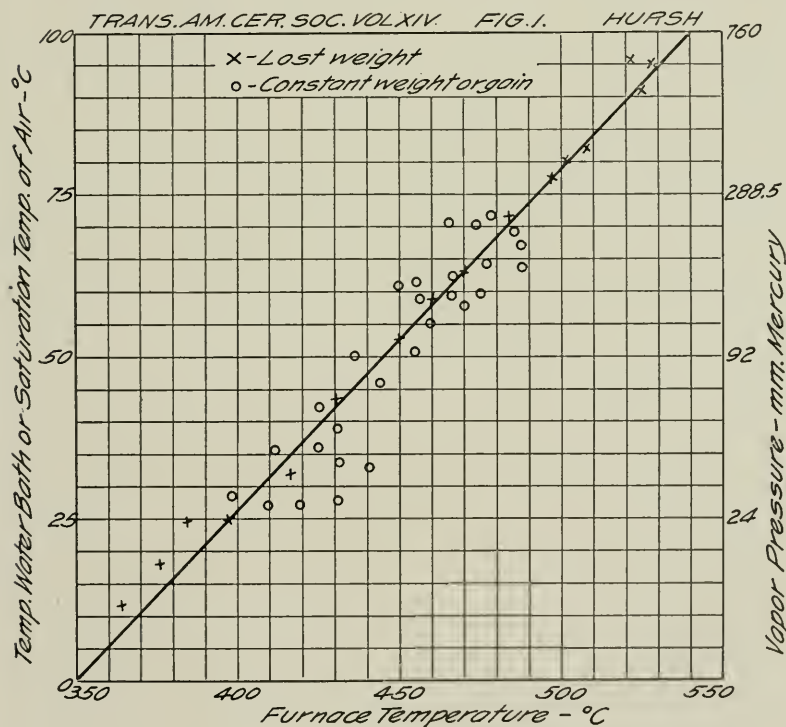
**AQUEOUS PRESSURES METHOD.**

Van Bemmelen, in studying the dehydration of the silicic acid gel, placed his samples in desiccators containing various concentrations of  $\text{H}_2\text{SO}_4$ . Constant temperature was maintained, and the samples were kept in the desiccators for sufficient time to reach equilibrium under the various vapor tensions. By plotting the loss of weight curve for the several concentrations of  $\text{H}_2\text{SO}_4$  or the corresponding vapor pressures, he was able to



determine the inversion points and the degrees of hydration in each case. The same method has been applied by Prof. A. V. Bleining<sup>6</sup> in studying the moisture in clays.

Dr. John Johnston<sup>7</sup> studied the dissociation pressures of several metal hydroxides and carbonates, using two experimental methods. The first was applied for hydroxides alone and is similar to one used by Brill. A small crucible containing a weighed portion (about 1.5 mg.) of the substance was suspended in a small electric furnace through which a current of air free from  $\text{CO}_2$  and of definite vapor pressure was passed. The air was freed from  $\text{CO}_2$  by passing through  $\text{NaOH}$ , then saturated with moisture by bubbling through a Liebig potash bulb, containing water, and



<sup>6</sup> Bulletin No. 7, Bureau of Standards.

<sup>7</sup> Ztschr. phys. Chem., LXII, p. 330.



was heated before passing to the furnace to prevent any condensation. The temperature of the water in the Liebig bulb was regulated by immersing it in a water bath. The furnace was held at constant temperature, and the vapor tension maintained at a definite value for 10 minutes by regulation of the water bath temperature. The crucible was then removed from the furnace and weighed on a very fine balance. Conditions of temperature and vapor pressure were so regulated that the substance maintained constant weight or gained slightly during the period, and these values were taken as the corresponding temperature and dissociation pressure of the material. The results of this method for  $\text{Ca(OH)}_2$  are shown in Fig. 1.

This method was found to be too slow and to frequently give inconsistent results. It was impossible to prevent the absorption of some  $\text{CO}_2$  while removing the crucible from the furnace for weighing.

#### STATIC METHOD.

Dr. Johnston then resorted to the "static method," in which the dissociation pressures are measured directly. A diagram of the apparatus is shown in Fig. 2. A platinum tube, P, about 5 cm. long and 4 mm. inside diameter, contained the substance. This tube was placed in a small electric furnace with a thermocouple for determining the temperatures. A piece of glass tube, C, was fused to P and to one arm of a U tube which was connected to the barometer. On each arm of the U tube was a bulb, L, bent to the side and holding enough mercury to fill the U-tube to a depth of about 3 cm. To prevent condensation of the vapor from P, the U-tube and C were enclosed by a glass steam jacket.

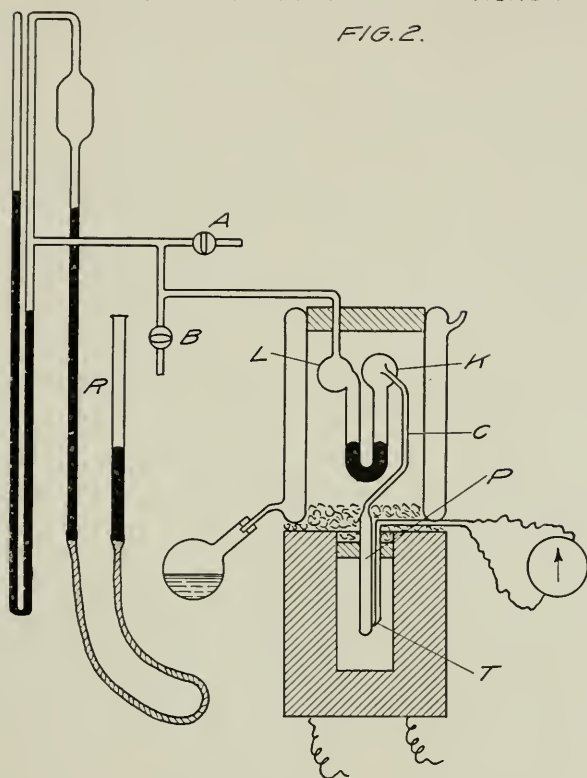
With the mercury in bulb L, the apparatus was exhausted through A by means of a mercury pump. Cock A was then closed, and the mercury run from L into the U-tube by tilting the apparatus. Heating was begun, and at the first indication of pressure in P, the mercury in the two arms of the U-tube was brought to the same level by admitting some air at B and adjusting by means of the leveling tube R.

In his work with calcium hydroxide, Dr. Johnston slaked pure  $\text{CaO}$  and absorbed the excess water in a desiccator. Another portion was made by allowing the  $\text{CaO}$  to absorb moisture

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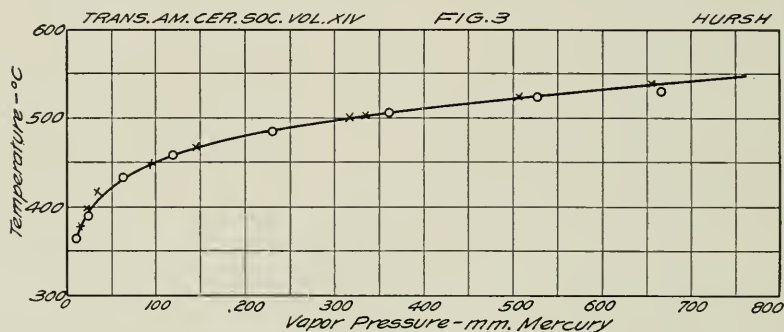
HURSH

FIG. 2.



slowly until the composition was about  $\text{CaO } 0.8\text{H}_2\text{O}$ . In using this substance, it was found necessary to heat it slightly during exhaustion of the apparatus since pressures of several cm. appeared between  $200^\circ$  and  $300^\circ$  which again disappeared in part on further heating. These abnormal pressures were supposedly due to loosely combined or absorbed moisture, and upon their appearance the test was stopped and the apparatus again exhausted. Only such pressures were taken as appeared at definite temperatures on heating and again disappeared on cooling. The "abnormal pressures" disappeared only partly on cooling. Under these conditions, it was found advisable to use a mixture of  $\text{CaO}$  and the hydroxide, although this did not entirely eliminate

the trouble, which was noted with all of the hydroxides studied. The results of the work on  $\text{Ca}(\text{OH})_2$  by this method are shown in Fig. 3. By the curve, it is seen that the dissociation pressure



reaches 760 mm. at a temperature of  $547^{\circ}\text{C}$ . Hence this is taken as the dissociation temperature of the substance under atmospheric pressure.

In studying zeolites Friedel<sup>8</sup> heated them at successively higher temperatures in a current of air of approximately constant vapor pressure. This method was adopted by Allen and Clement<sup>9</sup> in their study of tremolite, using dry instead of moist air. A crucible containing the material was placed in an electric furnace, through which a current of air, dried by concentrated  $\text{H}_2\text{SO}_4$ , was passed. After heating for some time at a definite temperature, the crucible was quickly removed to a desiccator, cooled and weighed. Heating was continued at each temperature until practically constant weight was obtained. In one case, the experiment was repeated with moist air to determine the effect upon the results obtained by using dry air.

#### EXPERIMENTAL WORK.

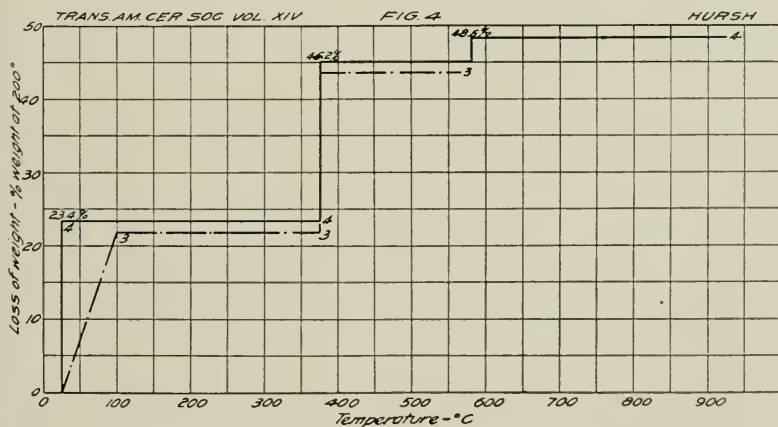
This method was adopted for the present work. The hydrate was prepared by calcining pure  $\text{CaCO}_3$  at  $1050^{\circ}\text{C}$ . and slaking the oxide with a slight excess of water. A portion of the hydrate was placed in a platinum crucible and heated in an

<sup>8</sup> Ztschr. phys. Chem., XXVI, p. 323.

<sup>9</sup> Am. Jour. Sci., Vol. XXVI, No. 152.

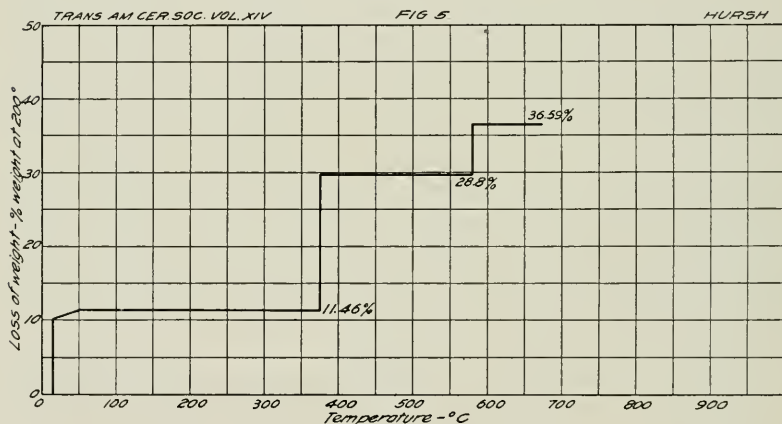
electric furnace in a bath of dry air, free from  $\text{CO}_2$ , at successive temperatures from  $200^\circ$  to  $750^\circ$  C. at  $50^\circ$  intervals. At 30-minute intervals, the crucible was removed from the furnace and cooled in a desiccator over concentrated  $\text{H}_2\text{SO}_4$ . The heating was continued at each temperature until constant weight was reached. It was impossible to prevent the absorption of some  $\text{CO}_2$  during the transfer of the hot crucible from the furnace to the desiccator. The first loss of weight was noted at  $400^\circ$  C. Continued heating at this temperature gave a total loss of weight of 77 per cent. of the water present above  $200^\circ$  C. At  $650^\circ$  another loss of weight took place amounting to 22 per cent. A second trial was made with  $10^\circ$  intervals from  $350^\circ$  to  $400^\circ$  C., and the first loss was found to take place at  $380^\circ$  C.

To prevent the absorption of  $\text{CO}_2$  by the sample, a method of weighing within the furnace was adopted. A platinum crucible was suspended in the furnace by a fine platinum wire from one pan of a balance that was carefully protected from unequal heating from the furnace. A thermocouple was placed with the junction just under the middle of the crucible. A current of air, free from  $\text{CO}_2$  and dried by  $\text{CaCl}_2$  and  $\text{P}_2\text{O}_5$ , was circulated through the furnace. A weighed portion of the hydrate was placed in the crucible and dried at  $25^\circ$  C. The temperature was then raised gradually until a loss of weight began at  $375^\circ$  C. It was somewhat surprising that there was no loss of weight be-



tween  $25^{\circ}$  and  $375^{\circ}$  as some mechanically held water might be expected. After constant weight was reached at  $375^{\circ}$ , the heating was continued beyond the point noted by Johnston. The second loss of weight took place at  $580^{\circ}$  C. The loss of weight curves for several trials are shown in Fig. 4.

To determine whether the presence of moisture in the furnace would have any effect upon the results, the air current was saturated at  $0^{\circ}$  to  $1^{\circ}$  C. before passing through the furnace, giving a vapor pressure of about 5 mm. The loss of weight was found to occur at the same points as before but to proceed at a slower rate. The quantitative results differ somewhat, due possibly to the longer time required in the latter trial. The result of the trial is shown in Fig. 5.



The results of these experiments indicate the existence of two hydrates of  $\text{CaO}$ , the  $\text{CaO} \cdot \text{H}_2\text{O}$  dissociating at  $375^{\circ}$  C., leaving a lower hydrate which dissociates at  $580^{\circ}$  C., leaving  $\text{CaO}$ . That the loss of weight at each point is due to the dissociation of a chemical compound is shown by the shape of the curves. The break is abrupt with no gradual slope preceding it. If mechanical or dissolved water were being driven off, there would be a gradual loss of weight with increasing temperature.

#### SUMMARY.

Various temperatures are given for the dissociation of  $\text{Ca}(\text{OH})_2$  ranging from  $450^{\circ}$  by Le Chatelier to  $547^{\circ}$  C. by Johnston.

Using the "loss of weight" method, two dissociation points are found. The hydrate,  $\text{Ca(OH)}_2$ , dissociates at  $375^\circ$ , forming a lower hydrate that loses its  $\text{H}_2\text{O}$  at  $580^\circ \text{C}$ .

No mechanical water was driven off above  $25^\circ \text{C}$ .

In conclusion, the writer wishes to express his indebtedness to Professor A. V. Bleining for many valued suggestions in this work.





## NOTE ON THE RELATION BETWEEN PREHEATING TEMPERATURE AND VOLUME SHRINKAGE.

By R. K. HURSH.

### INTRODUCTION.

An extended study of the effect of preliminary heat treatment upon clays within a practical temperature range has been made by Professor Bleining.<sup>1</sup> Especial attention was given to the effect upon the volume shrinkage. A decided change in the properties of most of the clays was noted at temperatures of 200° to 300° C. They became more or less granular and decreased markedly in plasticity. There was a material decrease in the volume shrinkage and an increase in the amount of pore water. In a few cases, this change occurred at somewhat higher temperatures. One fine-grained, highly plastic clay, similar in behavior to bentonite, showed a considerable change in physical properties at 250°; but treatment at temperatures up to 400° failed to reduce the shrinkage to working limits.

Professor Orton,<sup>2</sup> in studying some tertiary clays which gave trouble in drying, found ordinary preheating temperatures to be ineffective. When the temperature was raised to 450°–510° C. the plasticity and shrinkage were reduced sufficiently to make the clay workable. Under the conditions of the tests the period of safe treatment at these temperatures was closely limited since the clays lost their plasticity entirely when kept a little too long in the dryer. As some time is required for heat to penetrate the clay it is possible that the temperature may have reached a higher point in the longer treatments than was indicated by the thermo-couple. The test, however, represents the practical conditions in a rotary dryer.

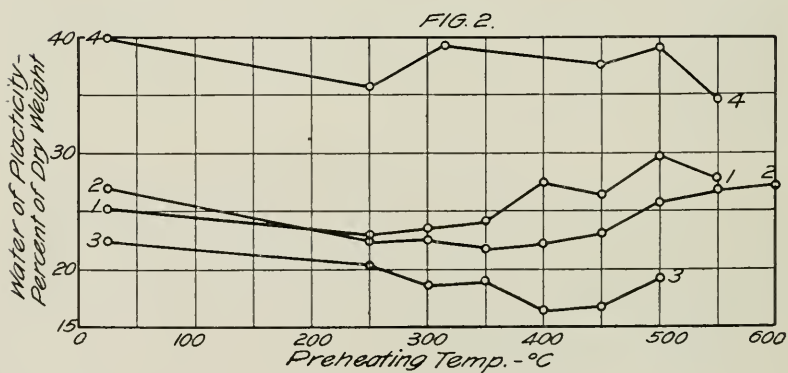
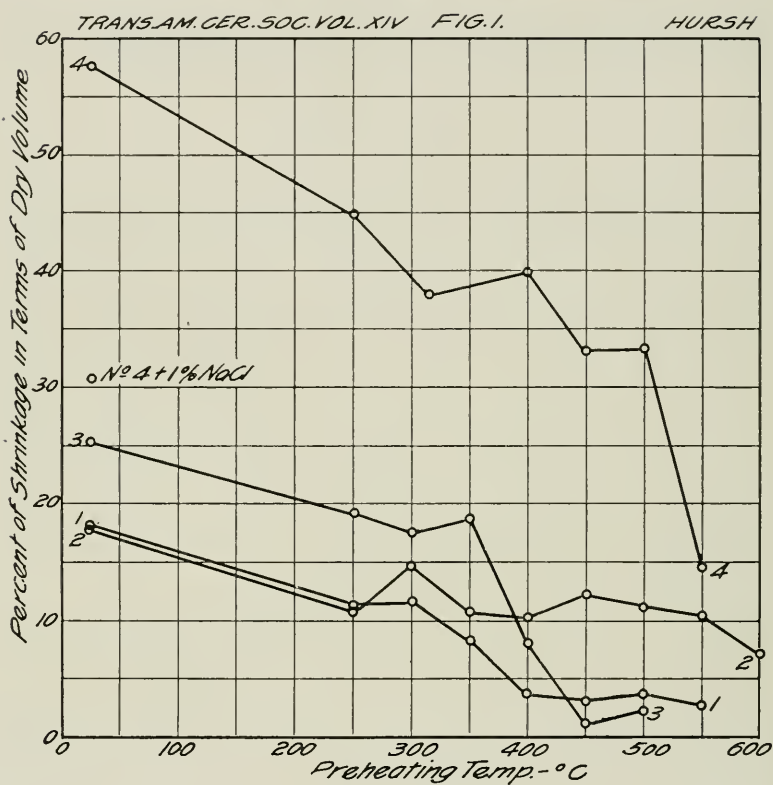
### EXPERIMENTAL WORK.

The present work was undertaken with the purpose of securing some further data upon the effect of the higher temperatures of preheating upon the physical properties of clays as indicated by changes in volume shrinkage. Four clays were used:

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<sup>1</sup> Bull. No. 7, Bureau of Standards.

<sup>2</sup> Trans. A. C. S., Vol. XIII, p. 765.



No. 1. A plastic, somewhat sandy surface clay from Urbana, Illinois.

No. 2. A plastic, red-burning shale from Danville, Ill.

No. 3. A plastic, No. 2 fire clay, having a high drying shrinkage, from St. Louis, Mo.

No. 4. A fine grained, weathered shale from Saskatchewan similar in character to the clays studied by Professor Orton. It became very sticky in the plastic state and cracked to pieces under any conditions of drying. It is of interest to note that the addition of 1 per cent. of NaCl greatly improved the working properties and reduced the drying shrinkage nearly one-half. It would be possible by this treatment to make commercial use of the material.

The clays were heated at temperatures  $50^{\circ}$  apart from  $250^{\circ}$  to  $650^{\circ}$  C. for three hours, from 1 to 2 hours being required to reach the temperature. They were then ground to pass 20 mesh and made up into small briquets. These were weighed and the volumes measured, dried in air and at  $110^{\circ}$  in an oven, weighed, immersed in coal oil for several hours and the dry volumes measured. Care was taken to get about the same consistency in the samples when making up the briquets. The shrinkage curves are shown in Fig. 1 and the moisture content in Fig. 2.

#### DISCUSSION OF RESULTS.

The surface clay, No. 1, changed in color from yellow to brown at  $250^{\circ}$  and to a light salmon-red at  $400^{\circ}$ . The plasticity was considerably decreased at  $250^{\circ}$ , was very low at  $400^{\circ}$ , the briquets being very friable, and was entirely gone at  $450^{\circ}$ . The color changes seem to correspond closely to the changes in volume shrinkage. Above  $300^{\circ}$  the shrinkage decreased rapidly to  $400^{\circ}$ , beyond which the heat treatment had little effect.

The shale, No. 2, changed from gray to brown at  $350^{\circ}$  and to red at  $400^{\circ}$ . The plasticity was considerably decreased at  $200^{\circ}$ , but decreased gradually from  $200^{\circ}$  to  $600^{\circ}$ . At  $650^{\circ}$  no plasticity remained, and the briquets were too fragile to handle. The shrinkage decreases very little from  $200^{\circ}$  to  $550^{\circ}$  but drops considerably at  $600^{\circ}$ .

The fire clay, No. 3, decreased in plasticity gradually up to

400°, but at 450° it became buff in color and was practically non-plastic. The effect of the heat treatment is much more marked than with the surface clay and the shale. The shrinkage curve drops very abruptly at 350°. The behavior of this clay is similar to that of an English ball clay studied by Professor Bleininger.<sup>1</sup>

The weathered shale, No. 4, changed in color from gray to deep maroon at 330°, at which point the cracking of the briquets was noticeably decreased but was still very bad. Cracking decreased gradually beyond this temperature, but the briquets at 550° were the only ones that remained sound with open-air drying. The sticky quality of the clay was retained up to 500°. At 550° it was quite granular but developed considerable plasticity with wedging. The effect of the heating treatment upon the shrinkage is more pronounced than with the other clays, but an abnormally high shrinkage remains 500°. Beyond this point the drop in the curve is so abrupt that very careful temperature control would be necessary in obtaining a sufficient reduction in shrinkage to prevent cracking without destroying the working properties. From the high temperature required and the narrow range of safe heat treatment, it is obvious that preheating would not be a safe method for practical use with such a clay.

The effect of the heat treatment upon these clays is quite different. The shale is most gradually affected, losing its plasticity entirely only at temperatures above red heat. It is probable that this is characteristic of the more homogeneous materials.

The fire clay shows an abrupt drop in its shrinkage curve, behaving similarly to other fire clays and a certain ball clay.

The fourth clay has such abnormally high shrinkage that only treatments above 500° C. would suffice to eliminate cracking in drying. It is evident that clays of this type are not adapted to preheating treatment.

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DEPARTMENT OF CERAMICS

A. V. BLEININGER, Director

## A THERMAL STUDY OF BORIC ACID-SILICA MIXTURES

BY

A. V. BLEININGER AND PAUL TEETOR

## THE REPLACEMENT OF TIN OXIDE BY ANTIMONY OXIDE IN ENAMELS FOR CAST IRON

BY

R. E. BROWN

1911-1912

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## A THERMAL STUDY OF BORIC ACID-SILICA MIXTURES.

By A. V. BLEININGER and PAUL TEETOR, Urbana, Ill.

The subject of possible chemical combinations of silica and boric acid has received some attention in our Transactions,<sup>1,2</sup> and the question raised is interesting inasmuch as such mixtures possess most decidedly the character of glasses or solid solutions. Thermal analysis thus does not promise a fruitful field of investigation. However, of the two methods comprising thermal analysis, the determinations of the softening temperatures is of some interest in itself, since it gives us the general character of the fusion curve of the two components involved.

A thermal lag is not to be expected either in the heating or cooling curves. In the present work, a search was made, however, for such a point based on the statement of Binns, Trans. A. C. S., X, p. 158, in which he records a temperature increase upon the fusion of a mixture of boric acid and silica, due to some exothermal change. The present research deals, (a) with the determination of the softening points of  $\text{SiO}_2\text{-B}_2\text{O}_3$  mixtures between the limits  $\text{B}_2\text{O}_3\text{-B}_2\text{O}_3\cdot 3\text{SiO}_2$ , (b) with the determination of heating and cooling curves and (c) with an investigation of the solubility of the fused glasses in water. The reagents used were chemically pure hydrous boric acid and silica, the latter being a B. & A. preparation which unfortunately contained several per cent. of sodium chloride and water. In the latter part of the series, fusions were made also with flint which had been passed through a 200 mesh sieve. The calculation of the mixtures was based upon the analyzed silica content, practically 97 per cent. The boric acid was fused, cooled rapidly and kept in a desiccator. It was crushed in a porcelain and pulverized in an agate mortar. Similarly, the silica was ignited and kept in a desiccator. The mixtures were ground together in the agate mortar and fused over the blast lamp in a 10 cc. platinum crucible kept covered during the heating. After some time, the yellow color of the mass disappeared, which seemed to be a measure of the completeness of the fusion. The cooled mass had an opaque

<sup>1</sup> Binns, Trans. A. C. S., Vol. X, p. 158.

<sup>2</sup> Singer, Trans. A. C. S., Vol. XI, p. 676.



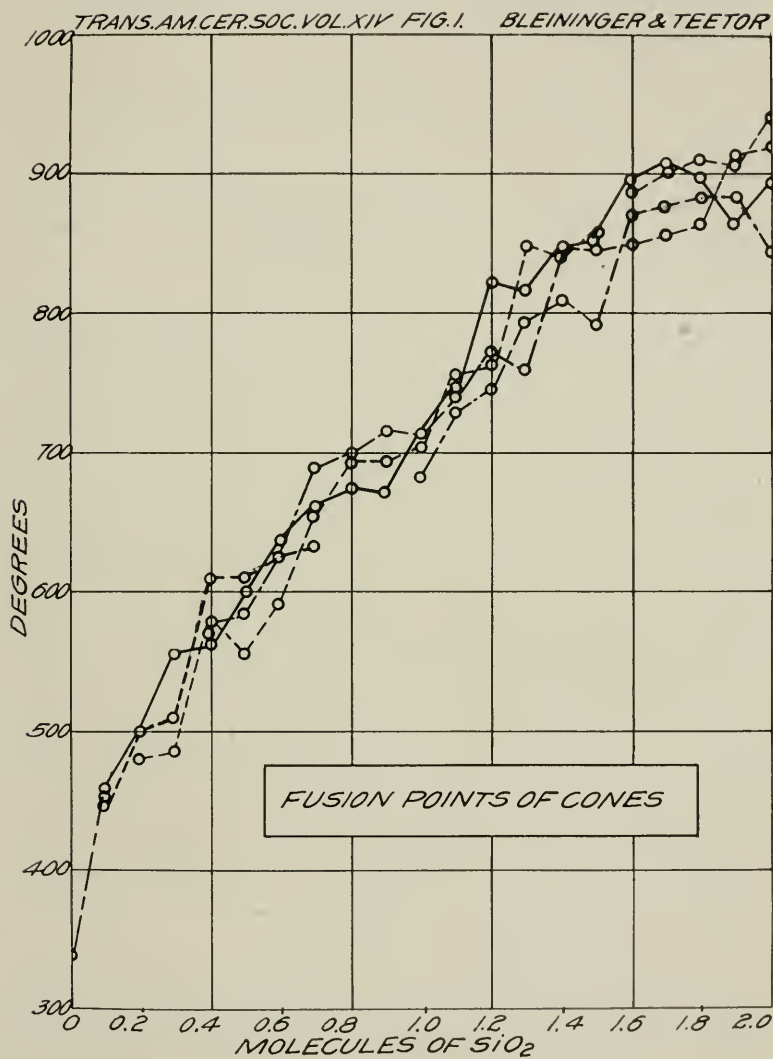
but glassy appearance. The fused mixture was easily removed from the crucible by inserting a platinum rod and quickly cooling in cold water. Then the fusion was pulverized and screened through 80 and 150 mesh screens. The portion passing the 80 but remaining on the 150 mesh screen was used for the solubility samples. This was done in order that no great variations in the surface factor might affect the solubility of the several mixtures.

#### SOFTENING POINT DETERMINATION.

For this purpose, the fused mixtures of  $\text{SiO}_2$  and  $\text{B}_2\text{O}_3$ , ground to a fine powder, were made up with a little water into small cones, and placed in an electric resistance furnace. The specimens were kept in position by means of platinum foil. Since in glasses practically no other criterion is available than the deformation point, the temperature at which the cones bent was taken to represent the softening point. Care was taken to raise the heat at a regular rate by rheostat regulation, and the temperature readings were made by means of a Pt-PtRd thermo-couple, the electromotive force of which was determined by the method of balancing against a standard cell by means of a potentiometer indicator.

Owing to the fact that by mistake water was used in making up the mixtures, some anhydrous boric acid reverted to the hydrous form. This, of course, made it troublesome to determine the deformation point of  $\text{B}_2\text{O}_3$  owing to the evolution of steam and the resulting bubbling. With the addition of 0.1  $\text{SiO}_2$ , the cones seemed to stand up apparently in good shape. The heat given off on adding water to the  $\text{B}_2\text{O}_3 \cdot 1.5\text{SiO}_2$  mixture was so great that the crucible could not be held in the hand. At the same time very little heat was evolved by the  $\text{B}_2\text{O}_3 \cdot 1.4\text{SiO}_2$  and the  $\text{B}_2\text{O}_3 \cdot 1.6\text{SiO}_2$  glasses. On fusing the  $\text{B}_2\text{O}_3 \cdot 1.5\text{SiO}_2$  mixture, it assumed a pink color.

It was soon observed that these glasses were quite viscous. This was illustrated by the fact that a twisted platinum wire on being lowered into the fused mass and again raised was found to draw out a ribbon of glass. It is not surprising, therefore, that the softening points could not be checked, in spite of the fact that the same rate of heating was followed as closely as possible.



In going over this part of the work four times, the results shown in Fig. 1 were obtained. The softening points of the mixtures beyond  $B_2O_3 \cdot 2SiO_2$  are not plotted since the divergence in this part of the series is still greater.

Softening point determinations were also made upon rods drawn from all of the fusions but these likewise gave extremely variable results, considerably lower than those obtained for the cones.

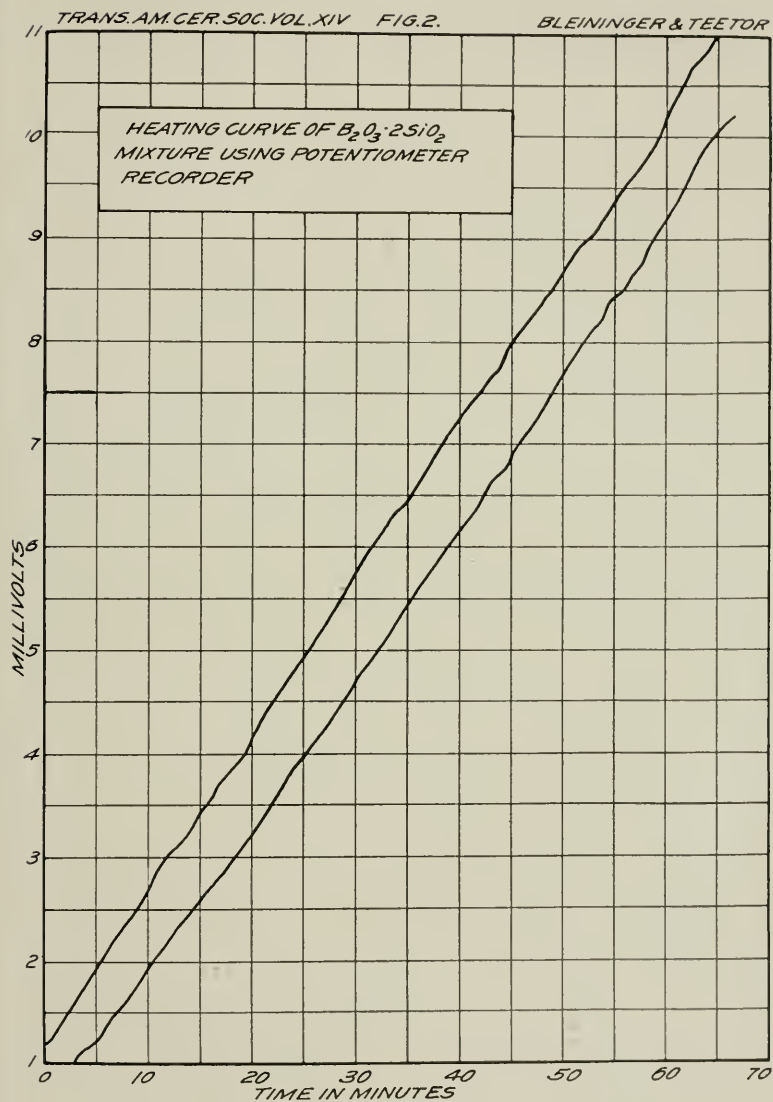
The evidence thus far collected makes it apparent that any reaction taking place under these conditions would be greatly hindered by the internal molecular friction.

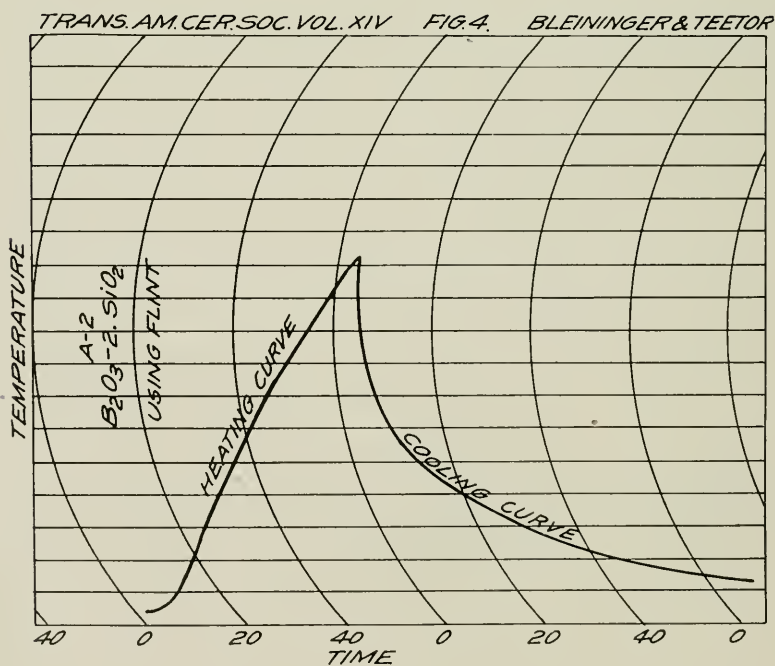
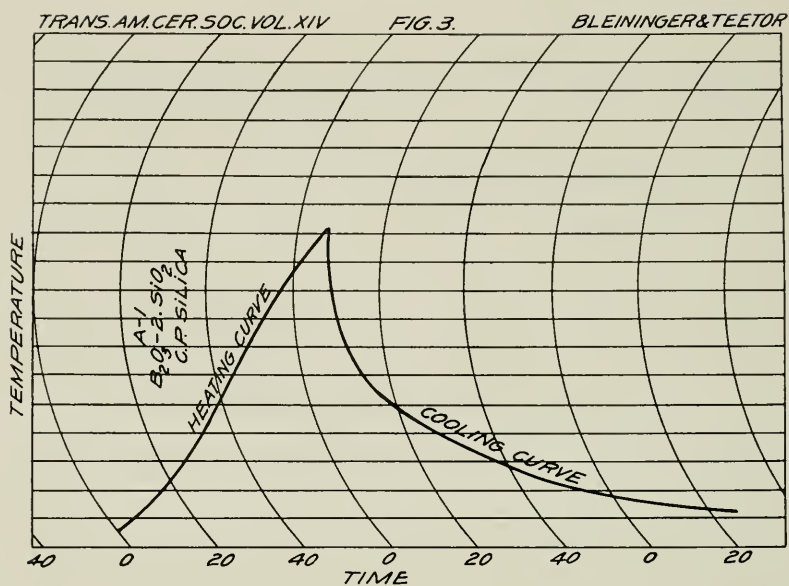
#### HEATING AND COOLING CURVES.

A considerable number of heating and cooling curves were determined with special reference to the  $B_2O_3 \cdot 2SiO_2$  mixture. The latter was prepared from fused  $B_2O_3$  and prepared  $SiO_2$ , and from fused boric acid and flint, passed through the 200 mesh sieve. In no instance was there a temperature acceleration or lag observed, and, hence, the observation of Binns was not checked. In Fig. 2, the heating curve in which the couple readings were made by means of a potentiometer indicator is shown. The junction was kept at  $0^\circ C.$  by means of ice. In Figs. 3 and 4, both the heating and cooling curves for prepared silica and flint mixtures as indicated by a Siemens and Halske recorder, making a contact every 16 seconds, are presented. It was observed that on fusing any mixture of  $B_2O_3$  and  $SiO_2$ , *without* previous fritting, some vapor was expelled suddenly, carrying evidently a certain amount of boron. This happened also when both the boric acid and silica had been ignited separately to constant weight before mixing. Since Professor Binns used an optical pyrometer, it is quite possible that by focusing upon this vapor the readings were changed as observed by him.

#### SOLUBILITY DETERMINATIONS.

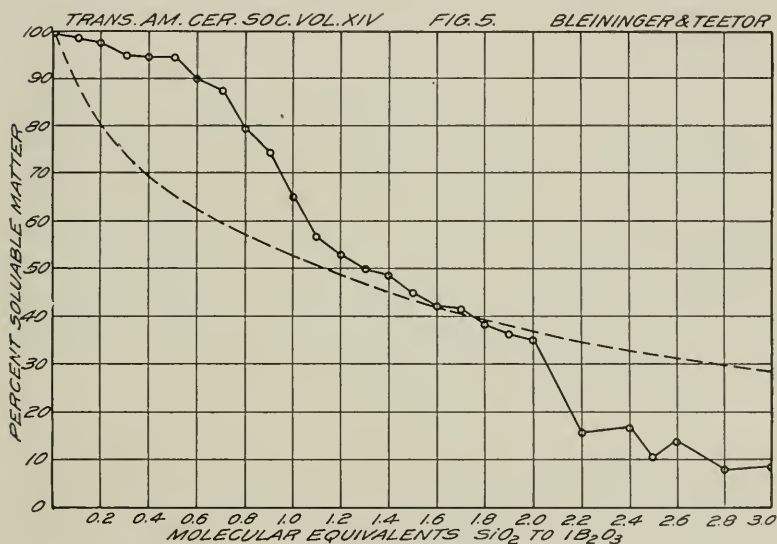
The different mixtures were fused and pulverized on cooling. The resulting powder was screened through the 80 and 150 mesh sieve. All material coarser than the 80 and finer than the 150 mesh was rejected. One gram samples were then weighed and put in stoppered 250 cc. Erlenmeyer flasks. These were placed





in a shaking machine together with 200 cc. of distilled water. After shaking for 10 hours and standing over night, the liquid was filtered off and the residue washed. Then 200 cc. of water was again added (including the wash water used) and the flasks were again shaken for one hour. The residue was again filtered and washed. After drying, the residues and paper were ignited and the weights determined. The insoluble matter in each case was brushed off and the paper burnt separately.

The weights of the residues are shown in the curve of Fig. 5.



It is seen that all of the boric acid was dissolved in the first of the series as well as some of the silica. At a point close to  $\text{B}_2\text{O}_3 \cdot 1.8\text{SiO}_2$ , however, the solubility curve crosses the line indicating the percentage content of  $\text{B}_2\text{O}_3$  (shown by the dotted line) which proves that some  $\text{B}_2\text{O}_3$  has been rendered insoluble. This tendency increases with the silica content. At the molecular ratio 1 : 2 a decided drop occurs indicating the rapid formation of an insoluble glass. As to the cause of this sudden change, we can only conjecture at the present time. To establish the fact that a chemical combination has taken place would require the

running of a parallel series using another criterion such as the specific gravity of the powder. At the present time, however, this evidence might be used to support the claim that we are dealing here with a solid solution representing a chemical union between the silica and the boric acid.

#### CONCLUSIONS.

Fused boric acid-silica mixtures are typical glasses possessing no definite deformation temperatures.

No thermal phenomena were observed, *i. e.*, there was no absorption or liberation of heat throughout the series  $B_2O_3$  to  $B_2O_3 \cdot 3SiO_2$ .

Boric acid when fused with silica first dissolves some of the latter. The amount of matter soluble in water decreases somewhat more rapidly than the  $B_2O_3$  content. Between 2 and 2.2  $SiO_2$  a decided drop in the solubility of the glasses occurs, indicating that some  $B_2O_3$  has been rendered insoluble. It is quite probable, although not proven, that a chemical combination might take place at this point. The gradual decrease in solubility might thus be ascribed to the formation of some of this combination at an earlier stage. At the point mentioned, a more rapid enrichment would thus take place.

#### DISCUSSION.

*Professor Binns:* I am interested in the results secured by Professor Bleining. When I made the first experiments of this kind I expressly disclaimed any pretension to the ability called for by such work, and I based my chief claim as to the action of boron upon the practical issues as expressed in glaze composition. From this position, which has been confirmed by Dr. Singer and Mr. Stull, I have not had cause to retreat.



## THE REPLACEMENT OF TIN OXIDE BY ANTIMONY OXIDE IN ENAMELS FOR CAST IRON.<sup>1</sup>

By R. E. BROWN, Mt. Savage, Md.

### INTRODUCTION.

**Classification of Opacifiers.**—Opacifiers for the purposes of this work are divided into two classes: (1) partial opacifiers, and (2) absolute opacifiers.

In the first class are included bone ash, fluorite, cryolite, and silica. Bone ash is rarely employed in enamels, but the remaining three, especially the silica, are invariably used. Fluorite and cryolite are advantageous, commercially, both from the standpoint of their low fusibility and their fluorine content. The latter gives them the property of acting as weak opacifiers, thereby decreasing the amount of absolute opacifier needed.<sup>2</sup> The silica, as is shown by the following work, has no opacifying tendencies in itself in this type of glasses but emphasizes and increases the opacity brought about by certain opacifiers proper.

In the second class, the opacifiers, *per se*, are arsenious oxide, zirconium oxide, tin oxide and antimony oxide. Arsenious oxide finds a very limited use, being employed only for decorative work on jewelry and art ware. Zirconium oxide is not widely used; while some consider it too expensive for commercial work, others regard it a cheap opacifier as a substitute for tin oxide.<sup>3</sup> Tin oxide is by far the most widely used of the opacifiers, and is employed not only in the enameling of sheet iron and cast iron, but in the enameling of clay products as well.

Antimony oxide has had, to date, only an extremely limited use as an opacifier. It has been used to some extent in Germany in conjunction with zinc oxide as a substitute for tin oxide.<sup>4</sup> It has been used in this country to some extent, and in one case its use in conjunction with other ingredients is patented as "a substitute for tin oxide."<sup>5</sup> In a "Note on White Antimony

<sup>1</sup> Abstract of a thesis fulfilling part of the requirements for the degree of Bachelor of Science in Ceramics, University of Illinois.

<sup>2</sup> Mayer and Havas, *Sprechsaal*, XLII, 460-461.

<sup>3</sup> *La Ceramique*, 11, 100-101. *Keram Rundschau*, XVI, 89-91, 135-139.

<sup>4</sup> Ph. Eyer, *Stahl und Eisen*, XVIII, 1097, 1099.

<sup>5</sup> U. S. Patent, 932,839.

Enamels," Bock points out the dangers of the use of antimony oxide in enamels for cooking vessels, but no mention is made of its employment in enamels for cast iron.<sup>6</sup>

The most expensive constituent of the ordinary commercial enamel is the opacifying agent, tin oxide, both by reason of the high market price and the quantity employed. The prices of antimony oxide and tin oxide in barrel lots are at present  $10\frac{1}{2}$  and 45 cents per pound, respectively.

**Object of Work.**—It was with a view to using the cheaper opacifier for cast iron enamels that this work was undertaken. The work attempts to determine, in a practical way, the conditions under which antimony oxide may be used in enamels.

#### EXECUTION OF WORK.

**Preparation of the Enamels.**—In carrying out a series the ingredients of the two extremes of a series were weighed up and mixed thoroughly by passing 5 or 6 times through a 20 mesh screen. The batch was next put into a small fire clay crucible (capacity about 250 grams of the raw batch) and fritted in a pot furnace, fired by a blast lamp using artificial gas and compressed air as fuel. After melting and becoming relatively free from bubbles the contents were poured into water. It was then dried, again put into the crucibles and refritted, care being taken in this second fritting to prolong the heating to such length of time that no bubbles were given off. As soon as bubbles had ceased to form, the contents were again quenched by pouring into water. The shattered glass was dried and then ground in 8 inch, porcelain, ball mills so as to pass a 200 mesh sieve.

The two extremes of a series, now in a powdered form, were weighed out in the proper proportions to form the intermediate enamels. These were now mixed by rubbing 5 or 6 times through a 60 mesh sieve.

**The Ingredients.**—The raw ingredients employed in introducing the following constituents with the molecular weights used were as follows:

ZnO: Introduced as zinc oxide (81).

PbO: Brought in as red lead  $Pb_3O_4$  (685).

<sup>6</sup> Chem. Ztg., XXXII, 516-517.

BaO: Where employed, was brought in by barium carbonate (197).

CaO: Brought in by fluorite (78), whiting (100), and hydrated lime (74).

Na<sub>2</sub>O: Introduced as sodium carbonate (106), borax (382), and cryolite (210).

K<sub>2</sub>O: Brought in by potassium nitrate (101) and potash feldspar (557).

MgO: Brought in by magnesium carbonate (84) and magnesium oxide (40).

Al<sub>2</sub>O<sub>3</sub>: Potash spar (557) was used as the main source of alumina. Small amounts of cryolite, Na<sub>3</sub>AlF<sub>6</sub> (210) were also used.

B<sub>2</sub>O<sub>3</sub>: This was brought in by using borax (382) in the cover enamels and as borax and boric acid (62) in the ground coats.

SnO<sub>2</sub>: Brought in as tin oxide (150).

Sb<sub>2</sub>O<sub>3</sub>: Introduced as white oxide of antimony (288).

SiO<sub>2</sub>: Brought in as potash feldspar (557), and as flint (60).

In addition to the above ingredients, ammonium carbonate was used in some of the enamels of the later series. This volatilizes readily and serves as a clarifier of bubbles in the glass during fritting.

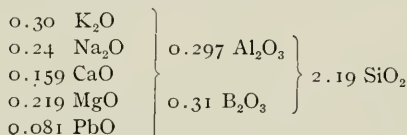
**Trial Pieces.**—The trial pieces were small circular discs  $\frac{1}{8}$ " thick and 2" in diameter with a raised center. The iron used for casting these trials did not prove to be of a very satisfactory grade as it frequently produced large bubbles or blisters in the enamels, probably due to the sulphur content of the iron.

The trials were cleaned by pickling for 20–30 minutes in a dilute solution of hydrochloric acid so as to remove the scale and any oxide present. After this they were washed and scrubbed and then dipped in a dilute solution of sodium carbonate so as to neutralize all of the acid. They were then scrubbed and washed again, the surface water was wiped off, and the trials were put into a warm oven. Even with this seemingly thorough treatment, the coat of carbon (left by dissolving the iron) was not entirely removed, and hence gave rise to bubbles during the burning process. Another method of cleaning the iron, used in the latter part of the work, proved very effective. In this, the iron

was pickled as before and then put into a ball mill with sand and water; thus all of the carbon was effectually removed with the result that less trouble as regards bubbling was experienced.

The ground coat was applied to the trials by dipping, care being taken to secure a thin coat that was as uniform as possible.

**Composition of the Ground Coat.**—The ground coat chosen was of the composition shown:



Batch weights: 15 flint; 30 potash feldspar; 10 boric acid; 5  $\text{KNO}_3$ ; 5  $\text{Pb}_3\text{O}_4$ ; 2.2  $\text{Ca(OH)}_2$ ; 2.3  $\text{MgO}$ ; 10.0 cryolite; 1.0 fluorite.

The trial piece, after being slush coated and dried, was placed in the furnace, which had been heated to the temperature of burning. As soon as the iron had attained a sufficient heat for fusing the ground enamel, it appears to "melt" not unlike a coat of frost or snow. This commences at one spot and soon has extended over the whole trial. The trial now has a glossy appearance. Almost coincident with this, innumerable bubbles are formed which "break" at once. This continues for a short time, after which the glossy coating or glass smooths down. It is at this point, in the writer's judgment, that the burning of the ground coat is complete. If the trial is not removed at once, larger bubbles are formed, but the glass is then decidedly more viscous than when the preliminary bubbles were formed. When they break, if they break at all, they leave a rough slag on the surface of the trial as is shown by cooling the trial piece.

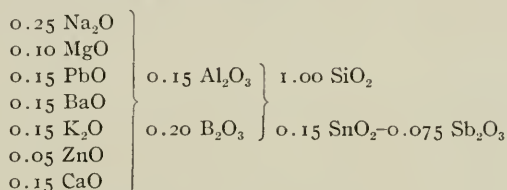
**Burning the Enamels.**—The furnace used for the enameling was of the open-fired type, *i. e.*, without a muffle chamber, and was fired by the use of artificial gas and compressed air as fuel. Although this is not the type of furnace best suited for this kind of work, it was the only one available and there was no time for the construction of a more suitable one. The temperature of burning was measured by a Le Chatelier pyrometer, the couple of which was inserted so that its junction point was at the side

of the trial. The holder for the trial piece consisted of a bar of iron "upset" at one end and so shaped as to fit on the inside of the trial piece.

### Series I.

#### REPLACEMENT OF TIN OXIDE BY ANTIMONY OXIDE IN A TIN ENAMEL.

This series was carried out by replacing the tin oxide in an enamel similar to that given by Riddle in his "Types of Enamels for Enameling Cast Iron Sanitary Ware," Trans. A. C. S., Vol. IX, with antimony oxide, thus:



Batch formulae (in equivalents).

No.	Na <sub>2</sub> CO <sub>3</sub>	R. Lead	BaCO <sub>3</sub>	CaF <sub>2</sub>	ZnO	MgCO <sub>3</sub>	Borax	K. Spar	Flint	SnO <sub>2</sub>	Sb <sub>2</sub> O <sub>3</sub>
1.....	0.15	0.05	0.15	0.15	0.05	0.10	0.10	0.15	0.10	0.15	0.00
2.....	0.15	0.05	0.15	0.15	0.05	0.10	0.10	0.15	0.10	0.1125	0.0188
3.....	0.15	0.05	0.15	0.15	0.05	0.10	0.10	0.15	0.10	0.075	0.0375
4.....	0.15	0.05	0.15	0.15	0.05	0.10	0.10	0.15	0.10	0.0375	0.056
5.....	0.15	0.05	0.15	0.15	0.05	0.10	0.10	0.15	0.10	0.00	0.075

**Description of Trials.**—No. 1 is a good enamel and is a typical tin enamel. All of the rest of the series, with the possible exception of No. 2, are very poor. A peculiar "puckery" or matte texture exists, the surface is rough and uneven, and the enamel flies off in patches, resembling shivering of clay ware. In the trials of enamels 3 and 4, the "puckery" effect is partially overcome by raising the burning temperature. The shivering is also lessened by this treatment. It is also evident in this series as well as in the rest of the work that where an enamel is applied, too thick shivering is more likely to occur.

Thinking perhaps that the "puckery" effect might be overcome partially by making a more easily fusible enamel it was



decided to run a series with a more fusible RO combination. It was also suggested that the "puckery" effect might be due to the barium which reacted with the sulphur present in the  $\text{Sb}_2\text{O}_3$ .<sup>7</sup> Some of the  $\text{Sb}_2\text{O}_3$  was tested and found to contain sulphur.

A series embodying the two above ideas was accordingly carried out as given below. Although it was not conducted strictly on a scientific basis it is sufficient to show in a practical way the desired effect.

### Series II.

VARIATION OF BARIUM OXIDE AND ITS EFFECT ON ANTIMONY OXIDE.

0.25-0.54 $\text{Na}_2\text{O}$	$\left. \begin{array}{l} 0.15-0.16 \text{ Al}_2\text{O}_3 \\ 0.20 \text{ B}_2\text{O}_3 \end{array} \right\} \begin{array}{l} 1.00 \text{ SiO}_2 \\ 0.075 \text{ Sb}_2\text{O}_3 \end{array}$
0.10-0.00 $\text{MgO}$	
0.15-0.15 $\text{PbO}$	
0.15-0.16 $\text{K}_2\text{O}$	
0.05-0.05 $\text{ZnO}$	
0.15-0.10 $\text{CaO}$	
0.15-0.00 $\text{BaO}$	

Batch formulae (in equivalents).

No.	$\text{Na}_2\text{CO}_3$	R. Lead	$\text{BaCO}_3$	$\text{CaF}_2$	$\text{ZnO}$	$\text{KNO}_3$	Cryolite	$\text{Ca(OH)}_2$	Borax	$\text{MgCO}_3$	Spar	Flint	$\text{Sb}_2\text{O}_3$
1.....	0.15	0.05	0.15	0.15	0.05	0.00	0.00	0.00	0.10	0.10	0.15	0.10	0.075
2.....	0.21	0.05	0.10	0.10	0.05	0.02	0.02	0.03	0.10	0.07	0.148	0.14	0.075
3.....	0.29	0.05	0.05	0.05	0.05	0.04	0.04	0.07	0.10	0.03	0.136	0.18	0.075
4.....	0.35	0.05	0.00	0.00	0.05	0.06	0.06	0.10	0.10	0.00	0.13	0.22	0.075

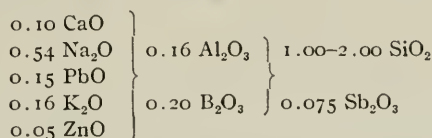
**Description of Trials.**—The "puckery" effect has decreased toward the end of the series which contains no barium and in No. 4 is not present at all. This enamel is a fair enamel which adheres well. No. 1 is somewhat shivered. This series shows from a practical standpoint that barium should not be used to any very large extent in an enamel where there is a contact with sulphur gases. Its use, however, in enamels where tin is used as an opacifier is very much desired, owing to its ability to decrease shivering.

<sup>7</sup>  $\text{Sb}_2\text{O}_3$  is prepared from stibnite,  $\text{Sb}_2\text{S}_3$ , by roasting in air, hence sulphates are formed which, if not entirely removed, would combine with the barium compounds.

## Series III.

## VARIATION OF THE SILICA CONTENT.

This series was varied between the limits of 1.00 and 2.00 equivalents of silica as shown:



Batch formulae (in equivalents).

No.	Na <sub>2</sub> CO <sub>3</sub>	R. Lead	ZnO	KNO <sub>3</sub>	Cryolite	Ca(OH) <sub>2</sub>	Borax	K. Spar	Flint	Sb <sub>2</sub> O <sub>3</sub>
1. ....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	0.22	0.075
2. ....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	0.345	0.075
3. ....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	0.47	0.075
4. ....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	0.595	0.075
5. ....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	0.72	0.075
6. ....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	0.845	0.075
7. ....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	0.97	0.075
8. ....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.095	0.075
9. ....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.22	0.075

**Description of Trials.**—Nos. 1, 2 and 3 have an egg shell-like texture but otherwise are fair enamels. The trials of enamels Nos. 4 and 5 are better and do not show the above texture to such a degree. No. 6 is a fair enamel but is a trifle dull. No. 7 is a good enamel and adheres well. It is whiter and has a better gloss than the average commercial enamel. Enamel No. 8 is whiter than No. 7 and has a better gloss. A few of the trials shiver somewhat, showing that the silica is a trifle too high. Enamel No. 9 has shivered still more, but on the trials where it held, it is the whitest and most brilliant of the series. Enamels Nos. 8 and 9 have an exceptionally white color and are more than the equal of the average tin enamel in this respect.

The result of this series seems to show that the last two enamels are too high in silica and also that a silica content of over 1.85 equivalents is conducive in shivering. The burning temperature rises as the silica content increases; but this heat,

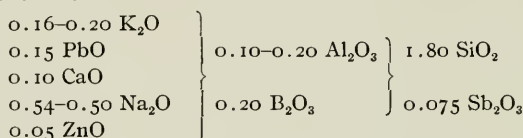


even with the enamels containing 2.0  $\text{SiO}_2$ , did not cause the iron to deteriorate to any visible extent. As silica increases, the whiteness is increased, and it is evident that a sacrifice must be made of part of the whiteness in order to obtain enamels that do not shiver.

### Series IV.

#### VARIATION OF ALUMINA.

This series was run between the limits of 0.1 and 0.2 equivalent of  $\text{Al}_2\text{O}_3$ . To bring in the  $\text{Al}_2\text{O}_3$  in combined form, *i. e.*, as spar, it was necessary to change the RO with respect to  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$  thus:



Batch formulae (in equivalents).

No.	$\text{Na}_2\text{CO}_3$	R. Lead	ZnO	$\text{K}_2\text{CO}_3$	$\text{KNO}_3$	Cryolite	$\text{Ca(OH)}_2$	Borax	K. Spar	Flint	$\text{Sb}_2\text{O}_3$
1. . .	0.35	0.05	0.05	0.06	0.06	0.06	0.10	0.10	0.07	1.38	0.075
2. . .	0.342	0.05	0.05	0.049	0.06	0.06	0.10	0.10	0.09	1.26	0.075
3. . .	0.334	0.05	0.05	0.038	0.06	0.06	0.10	0.10	0.11	1.14	0.075
4. . .	0.326	0.05	0.05	0.025	0.06	0.06	0.10	0.10	0.13	1.02	0.075
5. . .	0.318	0.05	0.05	0.013	0.06	0.06	0.10	0.10	0.15	0.90	0.075
6. . .	0.31	0.05	0.05	0.00	0.06	0.06	0.10	0.10	0.17	0.78	0.075

**Description of Trials.**—All enamels of the series are good enamels with whiteness increasing toward No. 6, *i. e.*, with increase of  $\text{Al}_2\text{O}_3$ . The temperature required for maturing increases, however, with the  $\text{Al}_2\text{O}_3$ . The best enamel of the series, taking burning temperature, whiteness, gloss, and adhesive properties into consideration, is No. 4 containing 0.16  $\text{Al}_2\text{O}_3$ .

### Series V.

#### VARIATION OF ANTIMONY OXIDE.

This series as well as the remaining two series was carried out in two parts, A and B, the two parts being practically alike

except for the silica content. Part B was carried out first and the limits of  $\text{Sb}_2\text{O}_3$  were not high enough, hence these were changed in A.

## Series V, A.

0.16 $\text{K}_2\text{O}$	$\left. \begin{array}{l} 0.16 \text{ Al}_2\text{O}_3 \\ 0.20 \text{ B}_2\text{O}_3 \end{array} \right\} \begin{array}{l} 1.8 \text{ SiO}_2 \\ 0.0-0.14 \text{ Sb}_2\text{O}_3 \end{array}$	
0.05 $\text{ZnO}$		
0.10 $\text{CaO}$		
0.15 $\text{PbO}$		
0.54 $\text{Na}_2\text{O}$		

## Series V, B.

0.16 $\text{K}_2\text{O}$	$\left. \begin{array}{l} 0.16 \text{ Al}_2\text{O}_3 \\ 0.20 \text{ B}_2\text{O}_3 \end{array} \right\} \begin{array}{l} 2.0 \text{ SiO}_2 \\ 0.0-0.11 \text{ Sb}_2\text{O}_3 \end{array}$	
0.05 $\text{ZnO}$		
0.10 $\text{CaO}$		
0.15 $\text{PbO}$		
0.54 $\text{Na}_2\text{O}$		

## V, A. Batch formulae (in equivalents).

No.	$\text{Na}_2\text{CO}_3$	R. Lead	$\text{ZnO}$	$\text{KNO}_3$	Cryolite	$\text{Ca(OH)}_2$	Borax	K. Spar	Flint	$\text{Sb}_2\text{O}_3$
1. ....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.02	0.00
2. ....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.02	0.02
3. ....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.02	0.04
4. ....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.02	0.06
5. ....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.02	0.08
6. ....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.02	0.10
7. ....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.02	0.12
8. ....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.02	0.14

## V, B. Batch formulae (in equivalents).

No.	$\text{Na}_2\text{CO}_3$	R. Lead	$\text{ZnO}$	$\text{KNO}_3$	Cryolite	$\text{Ca(OH)}_2$	Borax	K. Spar	Flint	$\text{Sb}_2\text{O}_3$
1. ....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.22	0.00
2. ....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.22	0.022
3. ....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.22	0.044
4. ....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.22	0.066
5. ....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.22	0.088
6. ....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.22	0.11

Description of Trials.—The trials of enamel 1 A have but

slight opacity. No. 2 A has a trifle more and so on up the series, Enamel No. 3 A has a fair opacity, No. 4 A and 5 A are good enamels, No. 5 A being the whitest. No. 6 A is a good enamel. It is whiter than No. 5 but is not quite so glossy. No. 7 is a good enamel and is a trifle "matte" in texture. No. 8 has a beautiful matte texture and differs from all the rest of the series in this respect. One of the trials, however, shows a tendency to shiver but this may possibly be due to the mode of application. Enamel No. 5 is the best of the A part of the series, taking gloss, finish, and general appearance into consideration, while for a dull or matte texture No. 8 is the best. Enamels No. 7 and 8 require a higher temperature for burning, thus indicating that high antimony decreases the fusibility.

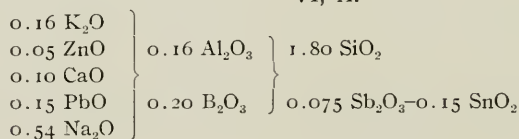
With part B of the series shivering is more evident in every case. The enamels which held are, however, of greater brilliancy and opacity, enamel No. 2 of A being identical in appearance with No. 1 of B. Enamels 2, 3 and 4 of part B are practically the same as 3, 4 and 5 of part A respectively. From this we would conclude that 0.016 equivalent of  $\text{Sb}_2\text{O}_3$ , in this range of silica content, has about the same opacifying effect as 0.02 equivalent of silica.

### Series VI.

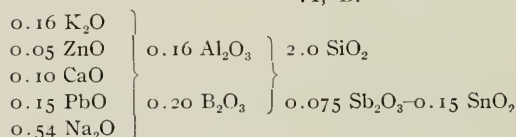
#### REPLACEMENT OF ANTIMONY OXIDE BY TIN OXIDE IN AN ANTIMONY ENAMEL.

This series, also using two different equivalents of silica, was carried out as follows:

##### VI, A.



##### VI, B.



Batch formulæ (in equivalents).

## VI, A.

No.	$\text{Na}_2\text{CO}_3$	R. Lead	$\text{ZnO}$	$\text{KNO}_3$	Cryolite	$\text{Ca}(\text{OH})_2$	Borax	K. Spar	Flint	$\text{Sb}_2\text{O}_3$	$\text{SnO}_2$
1. . . .	0.35	0.05	0.05	0.03	0.06	0.10	0.10	0.13	1.02	0.075	0.00
2. . . .	0.35	0.05	0.05	0.03	0.06	0.10	0.10	0.13	1.02	0.056	0.038
3. . . .	0.35	0.05	0.05	0.03	0.06	0.10	0.10	0.13	1.02	0.038	0.075
4. . . .	0.35	0.05	0.05	0.03	0.06	0.10	0.10	0.13	1.02	0.019	0.1125
5. . . .	0.35	0.05	0.05	0.03	0.06	0.10	0.10	0.13	1.02	0.00	0.15

## VI, B.

No.	$\text{Na}_2\text{CO}_3$	R. Lead	$\text{ZnO}$	$\text{KNO}_3$	Cryolite	$\text{Ca}(\text{OH})_2$	Borax	K. Spar	Flint	$\text{Sb}_2\text{O}_3$	$\text{SnO}_2$
1. . . .	0.35	0.05	0.05	0.03	0.06	0.10	0.10	0.13	1.22	0.075	0.00
2. . . .	0.35	0.05	0.05	0.03	0.06	0.10	0.10	0.13	1.22	0.056	0.038
3. . . .	0.35	0.05	0.05	0.03	0.06	0.10	0.10	0.13	1.22	0.038	0.075
4. . . .	0.35	0.05	0.05	0.03	0.06	0.10	0.10	0.13	1.22	0.019	0.1125
5. . . .	0.35	0.05	0.05	0.03	0.06	0.10	0.10	0.13	1.22	0.00	0.15

**Description of Trials.**—All enamels of the A part of the series adhere tenaciously and are good enamels. Enamel No. 1 has more opacity and whiteness than No. 5, these two properties decreasing uniformly between these extremes. The antimony enamel requires a slightly higher temperature for maturing, but not to such extent as to be detrimental to the iron.

In the B part of the series shivering is much in evidence, due to the increased silica. Enamels Nos. 1 and 2 have good opacity but Nos. 3 and 4 are much inferior in this respect. In enamel No. 5 the silica has dissolved the  $\text{SnO}_2$  almost entirely. Taking the results of this series we would conclude that  $\text{SiO}_2$  at the higher limit is opposite in effect with regard to  $\text{Sb}_2\text{O}_3$  and  $\text{SnO}_2$ . In the case of  $\text{Sb}_2\text{O}_3$  the opacity, whiteness and brilliancy are increased, while with  $\text{SnO}_2$  these properties, notably the opacity, are decreased. Shivering, however, is increased in either case. The results obtained in part A of the series are not in accord with those of Riddle whose high limit of silica was 1.25 equivalents. In enamel No. 5 part A as given above, a good white enamel was obtained using 1.8 equivalents of silica.

It might be interesting to note also at this point, the behavior of the enamels on wrought iron. The enamels of part A were applied to iron washers, and although they had not been

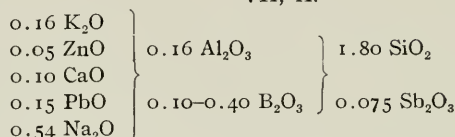
previously cleaned, the enamels held perfectly and were of good whiteness, brilliancy and texture.

### Series VII.

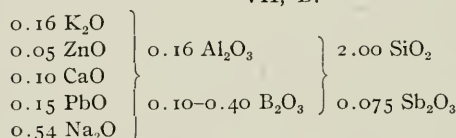
#### VARIATION OF BORIC OXIDE.

This series employs two equivalents of silica and the  $\text{Na}_2\text{CO}_3$  content is varied in order to reach the lower limit of  $\text{B}_2\text{O}_3$  still maintaining the same ratio.

#### VII, A.



#### VII, B.



#### VII, A.

##### Batch formulae (in equivalents)

No.	$\text{Na}_2\text{CO}_3$	R. Lead	ZnO	$\text{KNO}_3$	Cryolite	$\text{Ca}(\text{OH})_2$	Borax	K. Spar	Flint	$\text{Sb}_2\text{O}_3$
1.....	0.4	0.05	0.05	0.03	0.06	0.10	0.05	0.13	1.02	0.075
2.....	0.375	0.05	0.05	0.03	0.06	0.10	0.075	0.13	1.02	0.075
3.....	0.350	0.05	0.05	0.03	0.06	0.10	0.10	0.13	1.02	0.075
4.....	0.325	0.05	0.05	0.03	0.06	0.10	0.125	0.13	1.02	0.075
5.....	0.300	0.05	0.05	0.03	0.06	0.10	0.150	0.13	1.02	0.075
6.....	0.275	0.05	0.05	0.03	0.06	0.10	0.175	0.13	1.02	0.075
7.....	0.25	0.05	0.05	0.03	0.06	0.10	0.2	0.13	1.02	0.075

#### VII, B.

No.	$\text{Na}_2\text{CO}_3$	R. Lead	ZnO	$\text{KNO}_3$	Cryolite	$\text{Ca}(\text{OH})_2$	Borax	K. Spar	Flint	$\text{Sb}_2\text{O}_3$
1.....	0.4	0.05	0.05	0.03	0.06	0.10	0.05	0.13	1.22	0.075
2.....	0.375	0.05	0.05	0.03	0.06	0.10	0.075	0.13	1.22	0.075
3.....	0.350	0.05	0.05	0.03	0.06	0.10	0.10	0.13	1.22	0.075
4.....	0.325	0.05	0.05	0.03	0.06	0.10	0.125	0.13	1.22	0.075
5.....	0.300	0.05	0.05	0.03	0.06	0.10	0.150	0.13	1.22	0.075
6.....	0.275	0.05	0.05	0.03	0.06	0.10	0.175	0.13	1.22	0.075
7.....	0.250	0.05	0.05	0.03	0.06	0.10	0.200	0.13	1.22	0.075

**Description of Trials.**—All enamels of part A adhere well and are good white enamels up to No. 6. Nos. 6 and 7 have a yellowish cast and are not all desirable enamels. Bubbling is also evident in the enamels of higher  $B_2O_3$  content. Enamel No. 1 is the whitest of the five enamels.

The results obtained in part B are substantially the same as those of part A. The enamels are whiter, however, than the ones of the same  $B_2O_3$  content and the yellowish cast of enamels 6 and 7 of part A has disappeared in the corresponding enamels of part B. Shivering is present to quite a large extent in part B, due to the high silica. As in part A, bubbling is prominent in the enamels of the higher  $B_2O_3$  content. The difference in whiteness of the high and low  $B_2O_3$  enamels in part A is not so pronounced in this part of the series. Enamels B 1 and B 7 have very little difference in whiteness, B 1 being a little the whitest. The difference in maturing temperature is however quite large and the tendency to bubbling is more evident.

The results indicate that the lower the  $B_2O_3$  the better and whiter are the enamels. The limits for desirable enamels are about 0.15–0.30  $B_2O_3$ .

#### LIMITS OF THE INGREDIENTS.

The limits of the ingredients and their effects established by this work are as follows:

$SiO_2$ : The effect of silica is to increase brilliancy, whiteness, acid-resisting properties and gloss. If increased too high, shivering takes place and the maturing temperature is too high. The limits are about 1.65–1.85 equivalents, those nearer the higher limit being the preferable.

$Al_2O_3$ : Increased  $Al_2O_3$  increases the temperature for maturing and gives whiter enamels. The high limit is around 0.18 equivalent. The low limit was not established but for commercial enamels is probably about 0.13 equivalent.

$Sb_2O_3$ : The effect of  $Sb_2O_3$  is to increase the maturing temperature, and to increase the whiteness and opacity when employed between the limits of 0.0–0.09 equivalent  $Sb_2O_3$ . If used between the limits of 0.1–0.14 equivalent the enamels are dull at the lower limits and matteness increases at the higher.



At the high limit, 0.14 equivalent, shivering is likely to occur.

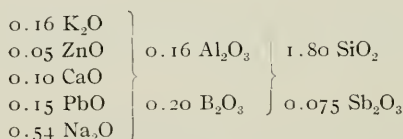
For brilliant enamels of good opacity and texture the limits are 0.06–0.09 equivalent, about 0.075 being preferable.

$\text{SnO}_2$ : No variation of the  $\text{SnO}_2$  content was made but a good enamel was obtained using 0.15 equivalent of  $\text{SnO}_2$ .

$\text{B}_2\text{O}_3$ : The effect of increased  $\text{B}_2\text{O}_3$  is to lower the maturing temperature, to increase the tendency to produce bubbles, to decrease the whiteness when used above a certain limit, increase gloss, and to increase the solubility of the enamel. The limits are about 0.15–0.3 equivalent, those nearer the lower limit being preferable.

$\text{BaO}$ : The effect of  $\text{BaO}$  in  $\text{Sb}_2\text{O}_3$  enamels is to produce a “puckery” or matte effect. This is no doubt due to the sulphur arising from the  $\text{Sb}_2\text{O}_3$  and the fuel gases, which comes in contact with the barium compounds.

The most likely enamel taking all points into consideration is:



#### DISCUSSION.

*Professor Staley*: Why do you not include the fluorine in your formula? No one will be able to calculate the batch from the formula unless you do so. Moreover, it makes a vast difference whether an enamel contains a small or a large amount of this element.

*Mr. Brown*: I do not think it is necessary. I introduced it as cryolite, using 0.06 equivalent of cryolite throughout.

*Professor Staley*: Mr. Brown, I just want to ask one more question. Did you get an absolutely pure white enamel, or was it of a greenish or bluish tint? There have been many attempts made to use antimony in place of tin oxide in cast iron enamels, but it has never given a satisfactory white. They get a tint they call white, but it is not a commercial white. Do you have any idea of how to avoid getting that greenish, bluish white so characteristic of antimony oxide?



*Mr. Brown:* I did not carry on work to eliminate the cast you speak of. The cast was not present to an aggravated extent that I could see. A number of others said the same thing. There is a slight bluish cast or tint in some of the trials.

*Professor Staley:* In your final enamel as well as in all the others?

*Mr. Brown:* It was not so pronounced in this case, but more so in the enamels of higher silica content.

*Mr. Burt:* I noticed in speaking of the enameled iron industry they always speak of dusting the enamel on and I would like to get a little description of what the mechanical process is—of what is involved in this dusting on of the glaze.

*Professor Staley:* In a paper ("The Manufacture of Enameled Iron Sanitary Ware," Trans. A. C. S., Vol. VIII, p. 172) I published several years ago, you can find a description of the ordinary method of making a piece of enameled cast iron. The only difference between the method described there and the method used at present is the use of a mechanical agitator.

*Mr. Burt:* What mesh sieve do you use?

*Professor Staley:* The sieve is a fifty- or sixty-mesh sieve.

*Mr. Brown:* I would like to ask Professor Staley what his opinion is of the fluorine in a fused enamel—whether it is volatilized or whether it is retained in the enamel. I have read of several instances where they analyzed for fluorine and found it in the enamels in small quantities.

*Professor Staley:* That is all a matter, in my mind, of how hard, how long, and how hot you heat the enamel. You can volatilize it all, or you can have the larger portion of it stay in. If it is all volatilized you have no opacifying effect from the use of fluorides. In cast iron enamels that are heated or fritted in the ordinary length of time, the large bulk of fluorine stays in.

#### NOTE PREPARED AFTER READING THE PAPER.

*Professor Bleining:* It seems to me that Mr. Brown has solved his problem satisfactorily. He has accomplished two things, *viz.*, the production of a white enamel which compares favorably with the best tin enamels, in the opinion of impartial observers, and he likewise has shown clearly the kind of enamel

required for the use of antimony as an opacifier, which differs somewhat from the common type.

As regards the poisonous quality of antimony compounds, Rickmann, Sprechsaal, XLV, 115-117, says that during an experience of ten years the use of metasodium antimonate has not proven injurious. However, he points out that the antimony oxide compounds (tartar emetic, etc.) are poisonous. For cast iron enamels, therefore, the use of  $\text{Na}_2\text{Sb}_2\text{O}_3$  might be a perfectly feasible solution.





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BULLETIN No. 19

DEPARTMENT OF CERAMICS

R. T. STULL, Acting Director

## INVESTIGATION ON IRON ORE CEMENTS

BY

ARTHUR E. WILLIAMS

PUBLISHED BY THE UNIVERSITY OF ILLINOIS, URBANA

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1913-1914



## IRON ORE CEMENT.\*

By ARTHUR E. WILLIAMS.†

Iron ore cement is a product intended to be used in sea water work. This material is now manufactured in Europe under the name of Erz cement. According to Mr. William Michaelis, Jr.,‡ the process of manufacture is similar to that of Portland cement except that limestone and iron ore are used in place of limestone and clay. United States Consul Thackara§ gives a description of its manufacture as follows: Chalk, flintstone, and finely ground ferric oxide are used. The flint and iron are ground together, then mixed with the chalk and water and screened through a fine sieve. The screened product is clinkered in a rotary kiln and then ground. An average composition of iron ore cement, given by Michaelis is:

CaO.....	63.5 per cent	Al <sub>2</sub> O <sub>3</sub> .....	1.5 per cent
SiO <sub>2</sub> .....	20.5 "	MgO.....	1.5 "
Fe <sub>2</sub> O <sub>3</sub> .....	11.0 "	Alkali.....	1.0 "

The effect of sea water is undoubtedly two-fold. In the first place chemical reaction may take place between certain constituents of the cement and the salts in sea water, and, on the other hand, the mechanical action of the waves carrying large amounts of sand, freezing, thawing, and the varying pressure of the water due to tide help to injure the cement submerged in sea water. This work, however, will be confined to the chemical action of sea water, for the mechanical action is of minor importance unless the cement is weakened by chemical changes.

The reactions which take place between Portland cement and sea water are said to be of three distinct kinds. *First*, the action of MgCl<sub>2</sub> and MgSO<sub>4</sub> in sea water on the calcium hydrate formed during the hardening process of the cement, forming Mg(OH)<sub>2</sub>, CaCl<sub>2</sub>, and CaSO<sub>4</sub>. *Second*, the action of gypsum,

\* Under the direction of Mr. R. T. Stull.

† Urbana, Ill. A Thesis for the Bachelor of Science Degree in Ceramics, University of Illinois in 1910.

‡ Eng. News, Vol. 58, pp. 645-646.

§ United States Consular Reports, June, 1908.



$\text{CaSO}_4$  formed above, upon the calcium aluminates forming calcium sulpho aluminate. *Third*, the crystallization of the gypsum and calcium sulpho aluminate giving an increase in volume, thus causing the disintegration of the mortar.

That free lime is present in set Portland cements is well known. Lamine\* found 32 per cent of  $\text{CaO}$  in cement submerged in the Black Sea 15 years. Every analysis of a cement exposed to sea water shows a high percentage of  $\text{MgO}$ . Vicat† in 1840 showed this fact clearly, a cement, which was submerged in sea water for 6 months, was analyzed. A sample, taken from the surface exposed to the sea, showed 10.4 per cent  $\text{MgO}$  and 19.3 per cent  $\text{CaO}$  while the interior, which was not impaired, showed 1.87 per cent  $\text{MgO}$  and 31.33 per cent  $\text{CaO}$ .

A. Meyer‡ states that cement loses strength in sea water. The  $\text{MgSO}_4$  acting with the silicate of lime forms  $\text{Mg}(\text{OH})_2$  and calcium sulphate. The  $\text{CaSO}_4$  reacts with the calcium aluminates ( $\text{Al}_2\text{O}_3, x \text{CaO}$ ) of the cement, forming  $\text{Al}(\text{OH})_3 + 3 \text{Mg}(\text{OH})_2 + \text{CaSO}_4 + \text{CaCl}_2$ .

Charles J. Potter§ says that  $\text{MgSO}_4$  is the most active constituent in sea water on cement. He found that  $\text{MgCl}_2$  softens cement but causes no expansion. Potter says that it is now definitely believed that magnesium salts act on the feebly combined lime and alumina compounds which on taking up water of crystallization cause bursting of the concrete. He mixed calcined red brick clay with Portland cement clinker in proportions of 6 to 10. From this mixture briquettes were made and placed, together with Portland cement briquettes, in fresh water, sea water, and sea water to which 10 per cent  $\text{MgSO}_4$  was added. Both of these cements gained strength in fresh water. In salt water, the Portland cement briquettes began to fail after 5 weeks and were disintegrated after 5 years. These cements showed blistering after one year, which was followed by expansion and bursting. The red cement improved continually but took 8 weeks to obtain the maximum strength that the Portland cement had obtained in 5 weeks. In the 10 per cent solution of  $\text{MgSO}_4$ , the Portland cement tested 500 lb. in a month and then went

\* *Le Ciment*, 1901, pp. 111-691-81.

† *Iron Ore Cement*—The P. C. Co. of Ilemmoor, Hamburg, Germany.

‡ *Chemisches Central Blatt*, Vol. 73, p. 1368.

§ *Jour. Soc. Chem. Ind.*, Vol. 28.

back to zero in 1 year. The red cement began at 250 lb. and increased continually to 1015 lb. in 8 years. Mr. Potter says that the chemical combination of  $\text{CaO}$ ,  $\text{SiO}_2$ , and  $\text{Al}_2\text{O}_3$  and water is feeble and that probably accounts for the ability of magnesium in sea water to be so active.

The experiments of Dr. Michaelis\* and Le Chatelier† lead them to the conclusion that Portland cement suffers in solutions containing sulphuric acid salts, which applies to sea water. A double salt is formed composed of gypsum and calcium aluminate. This sulpho-aluminate,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO} + 3\text{CaSO}_4$ , is said to crystallize with 30 molecules of water, which process must be accompanied by considerable expansion. Le Chatelier says that "the main cause if not the sole cause, of the injuries which cements suffer under the action of sea water is the formation of calcium sulpho-aluminate."

Rebuffat‡ says on the contrary that sulpho-aluminates cannot exist in cements in sea water but agrees with Michaelis and Le Chatelier that calcium aluminates are the parts of cement most easily acted upon by salts in sea water.

It has been shown that calcium ferrates are formed similarly to the calcium aluminates and that alumina could be replaced by ferric oxide in Portland cement. Dr. Michaelis puts this knowledge into use with the idea of overcoming the disintegration in sea water. The result of this application is the Iron Ore cement of today.

Dr. Michaelis and the Royal Experiment Station of Charlottenburg have tested these cements in comparison with Portland cements in a very thorough manner. Mr. William Michaelis§ says in a paper read in the United States that tests of Erz cement and Portland cement were made with both neat and 3 to 1 mixtures which were placed in fresh water, sea water, and water containing five times more salt than sea water. In sea water, the Erz cement developed a much greater strength than the Portland. In the strong salt water, the strength of the Portland cement decreased rapidly while the Erz cement showed a steady gain. Briquettes were made of Iron Ore and Portland cement

\* *Ton Industrie*, 1896, p. 838.

† *Le Ciment*, 1901, p. 31-32.

‡ *Ton Industrie Zeitung*, 1901, p. 272.

§ *Eng. News*, Vol. 58, pp. 645-646.

which were placed in a salt solution of five times the normal strength of sea water under pressure of 15 atmospheres for a few days. This condition destroyed the Portland cement briquettes entirely, while the Iron Ore cement increased in strength.

The Royal Experiment Station conducted similar tests to the above but much more elaborate. Two Iron Ore and three Portland cements were made into prisms, using a 3 to 1 mixture of standard sand and cement. These prisms were placed in sea water and water containing five times the percentage of salts in ordinary sea water. In addition to this, these three solutions were allowed to act upon test pieces made of cement mixed with varied amounts of gypsum. All the Portland cement mortars disintegrated in the three- and five-fold salt solutions; all the Iron Ore cement mortars remained intact and sound.

United States Consul A. W. Thackara\* investigated this cement for use on the Panama Canal. The result of his investigations was the adoption of this cement for concrete work exposed to sea water. Another point in favor of this cement is the property of slower setting. The cement is weaker than Portland for the first week, but then gradually gains strength and exceeds that of Portland.

Publications of previous experiments do not show definitely the best composition for cements giving the greatest protection against sea water. With this idea in view, the following investigations were undertaken:

The outline of procedure in these experiments is as follows: Newberry's cement formula,  $x(3\text{CaO}, \text{SiO}_2) + y(2\text{CaO}, \text{Al}_2\text{O}_3)$ , was used as a basis. Assuming, according to Newberry, that  $\text{Fe}_2\text{O}_3$  could replace  $\text{Al}_2\text{O}_3$  and form  $2\text{CaO}, \text{Fe}_2\text{O}_3$ , a triaxial diagram was plotted (Fig. 1), the three members stationed at the three corners being  $3\text{CaO}, \text{SiO}_2$ ,  $2\text{CaO}, \text{Al}_2\text{O}_3$  and  $2\text{CaO}, \text{Fe}_2\text{O}_3$ . By blending these three members, cements could be obtained containing various amounts of the calcium aluminate and the calcium ferrate.

The batch weights of these three members were calculated and about 15 kg. of each were weighed up, using practically chemically pure materials. Whiting, flint, aluminium hydrate, and red oxide of iron were the only ingredients. These batches

\* *United States Consular and Trade Reports*, June, 1908.

were ground in a ball mill, then passed through a 200-mesh sieve; thus getting thorough mixing and a finely ground batch. The formulæ for the cements made are given in Table I.

The following cements, No. 19, 20, 21, 22, 23, 24, 25, 36, 37, 38, 39, 40, 42, 48, 49, 50, 51, 52, 53, 54, 58, 59, 60, 61, 62, and 65 on triaxial diagram were then weighed up, blunged thoroughly, and partially dried by pouring the slip into plaster molds.

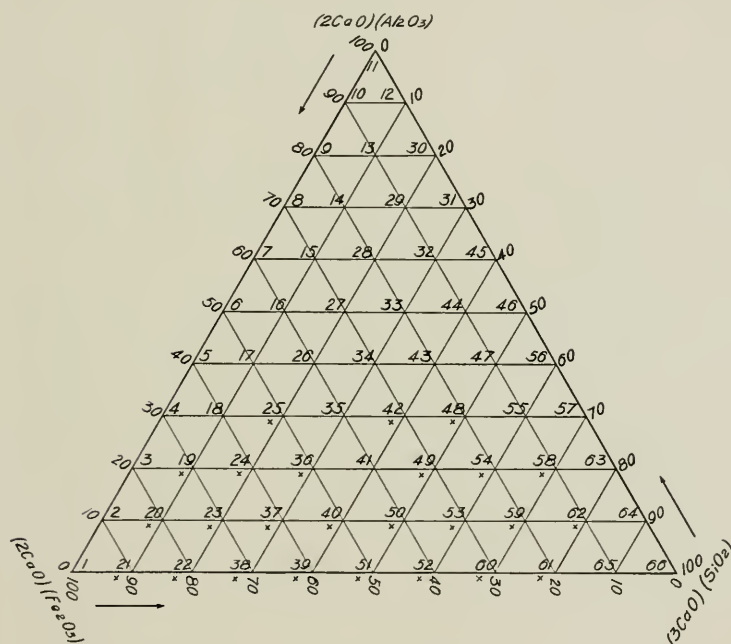


FIG. 1.—TRIAxIAL DIAGRAM.

The cements were then rolled into small balls about the size of a marble, dried, dehydrated in a down draft kiln to about 800° C. and placed in fruit jars ready for burning.

These cements were burnt in a magnesite test kiln, designed by Mr. Stull of the Ceramic Department, especially for burning experimental cements. The construction of this kiln is shown in Fig. 2. The success of this kiln is a noteworthy fact as test

kilns suitable for this purpose, heretofore, have not been very satisfactory owing to lack of control, unevenness of temperature in the clinkering chamber. Kerosene oil was used for fuel with an air pressure of about 50 lb.

The temperature at the time the clinker was drawn from the kiln was determined first by means of a Wanner pyrometer. This was given up, however, as the rapid rate of burning required a higher temperature than the true temperature of clinker formation.

TABLE I.—FORMULÆ OF CEMENTS MADE.

No.	Formulæ.	Molecular Ratio SiO <sub>2</sub> :AlO + Fe <sub>2</sub> O <sub>3</sub>
19	.1(3CaO, SiO <sub>2</sub> ) + 2(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 7(2CaO, Fe <sub>2</sub> O <sub>3</sub> ) .....	0.11
20	.1(3CaO, SiO <sub>2</sub> ) + 1(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 8(2CaO, Fe <sub>2</sub> O <sub>3</sub> ) .....	0.11
21	.1(3CaO, SiO <sub>2</sub> ) + 9(2CaO, Fe <sub>2</sub> O <sub>3</sub> ) .....	0.11
22	.2(3CaO, SiO <sub>2</sub> ) + 8(2CaO, Fe <sub>2</sub> O <sub>3</sub> ) .....	0.25
23	.2(3CaO, SiO <sub>2</sub> ) + 1(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 7(2CaO, Fe <sub>2</sub> O <sub>3</sub> ) .....	0.25
24	.2(3CaO, SiO <sub>2</sub> ) + 2(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 6(2CaO, Fe <sub>2</sub> O <sub>3</sub> ) .....	0.25
25	.2(3CaO, SiO <sub>2</sub> ) + 3(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 5(2CaO, Fe <sub>2</sub> O <sub>3</sub> ) .....	0.25
36	.3(3CaO, SiO <sub>2</sub> ) + 2(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 5(2CaO, Fe <sub>2</sub> O <sub>3</sub> ) .....	0.43
37	.3(3CaO, SiO <sub>2</sub> ) + 1(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 6(2CaO, Fe <sub>2</sub> O <sub>3</sub> ) .....	0.43
38	.3(3CaO, SiO <sub>2</sub> ) + 7(2CaO, Fe <sub>2</sub> O <sub>3</sub> ) .....	0.43
39	.4(3CaO, SiO <sub>2</sub> ) + 6(2CaO, Fe <sub>2</sub> O <sub>3</sub> ) .....	0.66
40	.4(3CaO, SiO <sub>2</sub> ) + 1(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 5(2CaO, Fe <sub>2</sub> O <sub>3</sub> ) .....	0.66
42	.4(3CaO, SiO <sub>2</sub> ) + 3(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 3(2CaO, Fe <sub>2</sub> O <sub>3</sub> ) .....	0.66
48	.5(3CaO, SiO <sub>2</sub> ) + 3(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 2(2CaO, Fe <sub>2</sub> O <sub>3</sub> ) .....	1.00
49	.5(3CaO, SiO <sub>2</sub> ) + 2(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 3(2CaO, Fe <sub>2</sub> O <sub>3</sub> ) .....	1.00
50	.5(3CaO, SiO <sub>2</sub> ) + 1(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 4(2CaO, Fe <sub>2</sub> O <sub>3</sub> ) .....	1.00
51	.5(3CaO, SiO <sub>2</sub> ) + 5(2CaO, Fe <sub>2</sub> O <sub>3</sub> ) .....	1.00
52	.6(3CaO, SiO <sub>2</sub> ) + 4(2CaO, Fe <sub>2</sub> O <sub>3</sub> ) .....	1.50
53	.6(3CaO, SiO <sub>2</sub> ) + 1(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 3(2CaO, Fe <sub>2</sub> O <sub>3</sub> ) .....	1.50
54	.6(3CaO, SiO <sub>2</sub> ) + 2(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 2(2CaO, Fe <sub>2</sub> O <sub>3</sub> ) .....	1.50
58	.7(5CaO, SiO <sub>2</sub> ) + 2(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 1(2CaO, Fe <sub>2</sub> O <sub>3</sub> ) .....	2.33
59	.7(3CaO, SiO <sub>2</sub> ) + 1(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 2(2CaO, Fe <sub>2</sub> O <sub>3</sub> ) .....	2.33
60	.7(3CaO, SiO <sub>2</sub> ) + 3(2CaO, Fe <sub>2</sub> O <sub>3</sub> ) .....	2.33
61	.8(3CaO, SiO <sub>2</sub> ) + 2(2CaO, Fe <sub>2</sub> O <sub>3</sub> ) .....	4.00
62	.8(3CaO, SiO <sub>2</sub> ) + 1(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 1(2CaO, Fe <sub>2</sub> O <sub>3</sub> ) .....	4.00
65	.9(3CaO, SiO <sub>2</sub> ) + 1(2CaO, Fe <sub>2</sub> O <sub>3</sub> ) .....	9.00

Almost all of these cements were fused till the surface was glassy in appearance before the cement seemed well clinkered and crystals appeared. Cements No. 54, 58, 62, and 65 appeared like a Portland clinker, except darker in color and were not fused or slag-like in appearance.

The clinker was first reduced in a jaw crusher and then ground in a disc mill; a screen test showed 24.2 per cent on 150 mesh screen; 12.3 per cent on 200 mesh screen; and the remainder, 63.5 per cent passed 200 mesh. These cements show that they are approximately of the same degree of fineness as the average Portlands. After the samples were ground, pats were made from



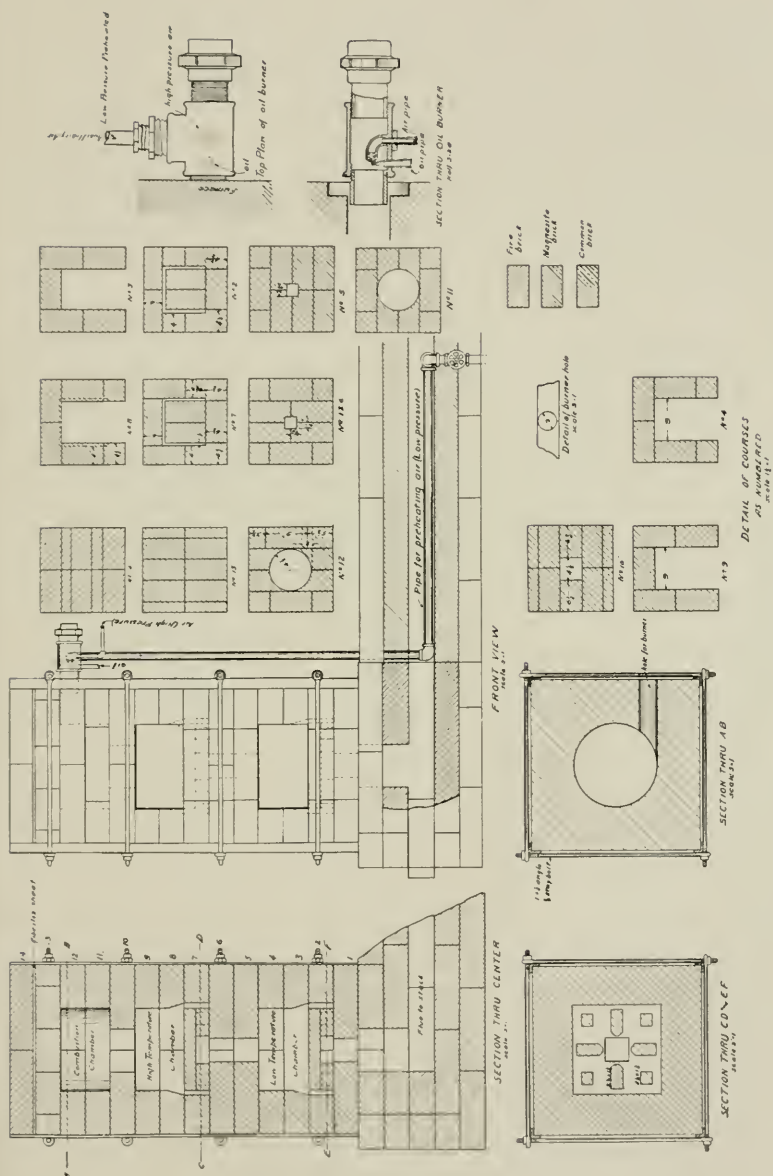


FIG. 2.—HIGH TEMPERATURE FURNACE FOR BURNING CEMENTS.

them in the usual manner to determine the properties of the cement.

The amount of water used for mortar was determined by the Boulonge method (Waterbury's Cement Manual, p. 44). The initial and final sets were determined with Gilmore needles.

Four pats were made of each cement with the idea of using one for the time of setting tests and placing the other three immediately in the moist closet, two of which were to be used for the boiling test after 24 hours, the third to be allowed to stand in

TABLE II.—RESULTS OF TESTS ON CEMENTS.

No.	Time of Initial Set, hours.	Time of Final Set, hours.	Water Used, per cent.	Remarks at Time of Final Set.	Conditions after 48 Hours in Moist Closet.
19	1½	3	21.0	Cracked in ½ hour	Cracked
20	1	5	20.0	O. K. Strong	Warped and crackedd
21	2½	5½	21.0	No cracks	No cracks
22	1½	4	20.0	Small cracks	No cracks
23	1	..	21.0	Cracked	No cracks
24	¾	5½	22.0	Cracked	No cracks
25	1¼	..	21.5	Cracked	No cracks. Soft
36	1¾	11	20.0	Cracked	O. K.
37	1	2½	20.0	Cracked	No cracks
38	1	5	20.0	O. K.	No cracks
39	2	8	21.0	Cracked	Cracked
40	1¼	3½	20.0	Cracked	Warped
42	½	2¾	21.5	O. K.	No cracks
48	1¼	7	22.0	O. K.	No cracks
49	1½	3	21.0	Cracked	Cracked
50	3	..	22.0	Cracked	No cracks. Soft
51	2	10	21.0	O. K.	Soft
52	1	9	20.0	Soft	Soft
53	1¼	4	21.0	Cracked	No cracks. O. K.
54	1	4¼	23.5	Cracked	No cracks. O. K.
58	1	3¼	22.0	No cracks	Cracked
59	½	4½	21.0	O. K.	Warped
60	1½	5	21.0	Soft and crumbly	Warped and crackedd
61	1	6	22.0	Warped	O. K.
62	1½	..	22.0	Did not harden	O. K.
65	1½	..	21.0	Cracked	Warped

water for 28 days. All of these cements went to pieces in cold water or in the boiling test. The results are given in Table II.

From these cements, one only, *i. e.*, No. 62, remained sound when placed in water. This cement also stood the boiling test (½ hr.), the others going to pieces. The molecular ratio of SiO<sub>2</sub> to Al<sub>2</sub>O<sub>3</sub> for this cement is four and since the molecular ratio for good cements is between 5.1 and 6.8 and since none of these cements lie between these limits, it was decided to construct a new group. Cement No. 62 approached these ratios nearer than any other.



A new batch was calculated after Bleining's formula  $(2.8\text{CaO}, \text{SiO}_2) + (2\text{CaO}, \text{Al}_2\text{O}_3)$  having different amounts of  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  and also the ratio of  $\text{SiO}_2$  to  $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$  varied from just above to just below the limits. The using of chemically pure raw materials in place of slag and limestone gives less efficient mixtures of lime and  $\text{SiO}_2$ . It was, therefore, thought that sufficient lime would be obtained by the use of Bleining's formula. For formulæ see Table III.

TABLE III.—FORMULÆ FOR CEMENTS MADE.

No.	Formulæ.
A <sub>1</sub>	5.1(2.8CaO, SiO <sub>2</sub> ) + (2CaO, Fe <sub>2</sub> O <sub>3</sub> )
A <sub>2</sub>	5.8(2.8CaO, SiO <sub>2</sub> ) + (2CaO, Fe <sub>2</sub> O <sub>3</sub> )
A <sub>3</sub>	6.4(2.8CaO, SiO <sub>2</sub> ) + (2CaO, Fe <sub>2</sub> O <sub>3</sub> )
A <sub>4</sub>	7.0(2.8CaO, SiO <sub>2</sub> ) + (2CaO, Fe <sub>2</sub> O <sub>3</sub> )
B <sub>1</sub>	5.25(2.8CaO, SiO <sub>2</sub> ) + 0.175(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + .825(2CaO, Fe <sub>2</sub> O <sub>3</sub> )
B <sub>2</sub>	6.00(2.8CaO, SiO <sub>2</sub> ) + .175(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + .825(2CaO, Fe <sub>2</sub> O <sub>3</sub> )
B <sub>3</sub>	6.40(2.8CaO, SiO <sub>2</sub> ) + .200(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + .800(2CaO, Fe <sub>2</sub> O <sub>3</sub> )
B <sub>4</sub>	7.22(2.8CaO, SiO <sub>2</sub> ) + .175(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + .825(2CaO, Fe <sub>2</sub> O <sub>3</sub> )
C <sub>1</sub>	5.44(2.8CaO, SiO <sub>2</sub> ) + .360(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + .640(2CaO, Fe <sub>2</sub> O <sub>3</sub> )
C <sub>2</sub>	5.80(2.8CaO, SiO <sub>2</sub> ) + .400(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + .600(2CaO, Fe <sub>2</sub> O <sub>3</sub> )
C <sub>3</sub>	6.40(2.8CaO, SiO <sub>2</sub> ) + .400(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + .600(2CaO, Fe <sub>2</sub> O <sub>3</sub> )
C <sub>4</sub>	7.00(2.8CaO, SiO <sub>2</sub> ) + .400(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + .600(2CaO, Fe <sub>2</sub> O <sub>3</sub> )

PERCENTAGE COMPOSITION.

No.	CaO	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Molecular Ratio R <sub>2</sub> O <sub>3</sub> :SiO <sub>2</sub>
A <sub>1</sub>	66.0	0.0	11.6	22.4	5.1
A <sub>2</sub>	66.7	0.0	10.4	22.9	5.8
A <sub>3</sub>	67.2	0.0	9.6	23.2	6.4
A <sub>4</sub>	67.5	0.0	8.9	23.6	7.0
B <sub>1</sub>	66.7	1.3	9.4	22.6	5.25
B <sub>2</sub>	67.4	1.1	8.4	23.1	6.00
B <sub>3</sub>	67.5	1.3	7.8	23.4	6.40
B <sub>4</sub>	68.1	0.9	7.2	23.8	7.22
C <sub>1</sub>	67.4	2.5	7.2	22.9	5.44
C <sub>2</sub>	68.0	2.7	6.0	23.3	5.80
C <sub>3</sub>	68.2	2.5	5.8	23.5	6.40
C <sub>4</sub>	68.5	2.3	5.4	23.8	7.00

These cements were prepared in the same manner except that the temperature of clinkering was determined as near as possible by the method used. The kiln was allowed to cool to about 1000 deg. C. before a batch of cement was put in and temperature was then gradually raised till clinker was formed, the temperature was then read with a Wanner pyrometer.

The clinkers obtained appeared exceptionally good, being dull black in color and glistening brightly in the sun. These

clinkers were pulverized the same as has been previously described, then tested.

The results of these tests, Table IV, show that good cements can be obtained with a large amount of alumina using the same ratio of  $\text{SiO}_2$  to  $\text{R}_2\text{O}_3$  as Portland cements require. One very noticeable fact, however, is that when no  $\text{Al}_2\text{O}_3$  is present as in series A,  $A_2$ ,  $A_3$ , and  $A_4$  these cements all show expansion, thus giving evidence of free lime. Although  $A_1$  stood the boiling test, the cubes made from this cement bulged out from the mold considerably.

The question arises at this point, is it always necessary for  $\text{Al}_2\text{O}_3$  to be present or can a good cement be made without it?

TABLE IV.—RESULTS OF TEST.

No.	Temperature when Clinkered, deg. C.	Time to Clinker, hours.	Appearance of Clinker.	Initial Set, hours.	Final Set, hours.	H <sub>2</sub> O, per cent.
$A_1$	1300	$3\frac{1}{4}$	.....	24	62	24.8
$A_2$	1320	$1\frac{1}{2}$	All	22	56	24.0
$A_3$	1320	$1\frac{1}{2}$	clinkered	26	56	23.2
$A_4$	1330	$\frac{1}{2}$	good,	28	60	26.0
$B_1$	1390	$1\frac{1}{2}$	colored black	$4\frac{3}{4}$	40	26.3
$B_2$	1320	$1\frac{1}{4}$	and	$4\frac{1}{2}$	44	24.4
$B_3$	1350	$\frac{3}{4}$	glistening	11	36	28.0
$B_4$	1400	$1\frac{1}{2}$	with	5	48	25.0
$C_1$	1320	$1\frac{1}{2}$	crystals	5	30	24.4
$C_2$	1320	$\frac{3}{4}$	in a	12	40	24.0
$C_3$	1330	$1\frac{3}{4}$	bright	12	48	28.0
$C_4$	1380	$\frac{1}{2}$	light	17	40	27.2

This ought to be possible by reducing the lime content, as  $A_1$  was the best of series A and also had the smallest amount of lime silicate.

The slowness of setting is another factor which must be considered. It will be seen by Table IV that all of the cements required a long time to harden. This must be carried on in a moist atmosphere also or the cement will dry out before it has completely hydrated and set. The above factors will perhaps limit the use of this cement to work under water which may be allowed to set a considerable time.

All the cements of series B stood a 6-hr. boiling test without showing any signs of expansion. In series C all but  $C_1$  stood the boiling test.  $C_1$  warped a little and came loose from the glass

plate although the cement has a comparatively low lime content and its formula lies between other good cements.

The attempt was next made to give these cements a comparative test with Portland cement to show their relative resistance to sea water. The method used was similar to that of Dr. Michaelis.

One-inch cubes were made of each series of cements together

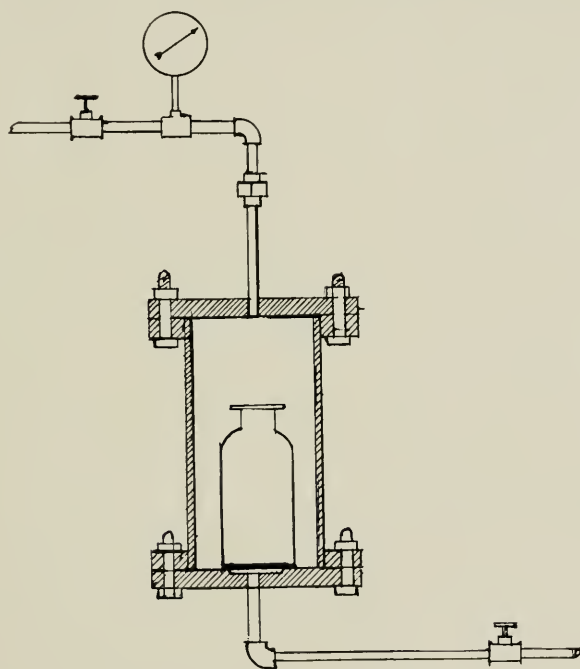


FIG. 3.—STEAM CYLINDER.

with a set of cubes of a standard commercial Portland cement, which had stood all the commercial tests. These were allowed to stand 60 hr. in the moist chamber and then placed in water, remaining in water for 27 days. The cubes made from series A together with a set of 5 Portland cement cubes were placed in a steam cylinder, Fig. 3, containing an artificial sea water solution of ten times normal strength. The quantity of salt is shown in Table V. The cements were then put under steam pressure

of 125 lb. or  $8\frac{1}{3}$  atmospheres, the temperature being between 150 and 200 deg. C. This was continued for 3 days. On opening the cylinder, the salt solution was found to be very dilute due to condensation of steam and no visible action on the cements had occurred. The salt solution and cubes were then put into a large wide-mouthed bottle, provided with a stopper and small vent hole. The bottle was then placed inside the pressure cylinder and steam admitted, allowing little or no condensation. After being sure that the bottle was not broken by the first change in temperature, the pressure was kept on for 3 days longer. Upon opening the cylinder, the cubes were found bone dry and covered with salt and the bottle cracked. This was due, no doubt, to the rapid reduction of the pressure, allowing the water

TABLE V.—ANALYSIS OF SEA WATER.\*

Salt.	Per cent of Salt.	Ten times per cent of Salt.	Total for 12 liters of Water.
NaCl.....	77.75	.....	342.10
MgCl <sub>2</sub> .....	10.87	108.7	478.28
MgSO <sub>4</sub> .....	4.73	47.3	208.12
CaSO <sub>4</sub> .....	3.60	36.0	158.40
K <sub>2</sub> SO <sub>4</sub> .....	2.46	.....	10.80
MgBr.....	0.217	.....	0.93
CaHCO <sub>3</sub> .....	0.345	.....	1.62

37.3 parts per thousand parts water.

100 parts = 2700 parts water.

12000

— = 4.4 factor times per cent of salt = quantity per 12 liters of water.

2700

to vaporize rapidly, which was at a temperature above its boiling point.

The results of this test were contrary to what was expected as the Portland cements were untouched and all of the iron cements were cracked and swollen. This cracking and swelling is caused, no doubt, by an excess of free lime, as these cements showed an expansion in the boiling test and there was a deposit of hydrated lime in the bottom of the cylinder which seemed to have been leached out of the cubes.

No crushing strength test of Series A was made as they were all destroyed already.

Series B was then placed in the cylinder, with a set of Port-

\* *University Geological Survey of Kansas*, Vol. 7, p. 27.

land cement cubes. A vessel made of 4-in. pipe was used in place of the glass bottle to overcome cracking due to sudden change in temperature. This series was kept under pressure for 6 days, and when removed from the cylinder neither the Portland or Iron Ore cements appeared harmed except cement  $B_3$  which went to pieces. The reason for the disintegration of this cement is unexplainable except that it was not clinkered properly. The boiling test, however, showed a good cement. (Table VI.)

As the crushing strength tests of the Portlands show, there seemed to be no weakening due to being in the salt solution.

TABLE VI.—RESULTS OF BOILING TEST FOR 6 HOURS, AFTER 60 HOURS IN MOIST CHAMBER.

Number.		Appearance after Sea Water Test.
$A_1$ .....	Good.	Cracked.
$A_2$ .....	cracked plate.	"
$A_3$ .....	Came loose from plate and showed some expansion.	"
$A_4$ .....	Same as $A_3$ .	"
$B_1$ .....	Good.	Sound.
$B_2$ .....	"	"
$B_3$ .....	"	Went to pieces.
$B_4$ .....	"	Sound.
$C_1$ .....	Came loose from plate, warped.	Cracked and swollen.
$C_2$ .....	Good.	Sound.
$C_3$ .....	Good.	"
$C_4$ .....	"	"

Also the strength of the Portlands seems to average higher than the Iron Ore cements. (Table VII.)

Five cubes of each cement of Series  $C$  were then placed into the cylinder with a set of Portland cubes made at the same time. These were kept under pressure for 8 days. The results of this series were quite different as 4 of the 5 cement cubes were badly cracked and had begun to swell.  $C_2$ ,  $C_3$ , and  $C_4$  showed no signs of disintegration, but  $C_1$  was cracked and swollen badly. This cement, as the  $A$  Series, did not stand the boiling test and such an action would be expected from it under the extreme conditions in the pressure cylinder. The crushing strengths of  $C_2$ ,  $C_3$ , and  $C_4$  averaged lower than the  $B$  Series,  $C_2$  was so soft that disintegration had evidently set in.

TABLE VII.—CRUSHING STRENGTH OF CEMENTS.

No.	Cross-sectional Area, sq. in.	Crushing Strength.		Average, lb. per sq. in.
		Total lb.	Lb. per sq. in.	
<i>P</i> <sub>1</sub> = Portlands in fresh water 3 weeks.				
<i>P</i> <sub>1</sub>	1.08	7680	7100	6042
	0.975	4780	4900	
	1.06	6650	6280	
	1.045	5650	4910	
	1.105	7750	7020	
<i>P</i> <sub>2</sub> = Portland cement in fresh water 4 weeks.				
<i>P</i> <sub>2</sub>	0.97	7850	8700	7876
	0.95	6620	6970	
	0.97	7730	7960	
<i>P</i> = pressure with Series <i>B</i> of the Iron Ore Cements.				
<i>P</i>	0.97	5420	5590	6920
	1.25	4860	3890*	
	1.025	7650	7470	
	0.98	7330	7470	
	1.01	7200	7150	
Iron Ore Cement in salt solution under pressure cylinder 6 days.				
<i>B</i> <sub>1</sub>	1.035	5810	5620	5241
	1.075	6720	6250	
	1.035	5120	4915	
	1.06	4740	4460	
	1.045	5200	4860	
<i>B</i> <sub>2</sub>	1.105	7170	6500	6616
	1.02	6620	6000	
	1.055	7500	7100	
	1.115	8430	7550	
	1.125	6680	5930	
<i>B</i>	1.09	4480	4120	5014
	1.075	5180	4820	
	1.10	5000	4540	
	1.06	6610	6240	
	1.12	6000	5350	
<i>C</i> <sub>2</sub>	1.025	4200	4080	4914
	1.03	5400	4360	
	1.025	6320	6660	
	1.1	5850	5310	
	1.04	4850	4660	
<i>C</i> <sub>3</sub>	1.05	2280	2190	2110
	0.97	1580	1660	
	1.1	2640	2400	
	1.00	1820	1880	
	1.01	2500	2480	
<i>C</i> <sub>4</sub>	1.07	5220	3000	5757
	1.07	6630	6150*	
	1.06	3630	3330	
	1.07	5140	4800	
	1.04	4050	3900	
Portlands in Cylinder 7 days with Series <i>C</i> .				
<i>P</i>	0.99	3000	3030	Only unaffected Portland cement cube.
<i>P</i>	0.97	6720	6930*	

\* Signifies not calculated in average.



## CONCLUSIONS.

As the time for this investigation was limited, further work could not be done, and the conclusions which may be drawn from these results are limited. This much may be said, however:

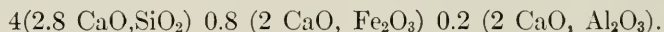
1. The amount of lime or silicate of lime ought to be less when  $\text{Fe}_2\text{O}_3$  alone is used in place of  $\text{Al}_2\text{O}_3$ , as the lowest ratio of Series A 5.1 was the only one which stood the boiling test. Series B showed that the limits gave good cements throughout, neglecting  $B_3$  which must have disintegrated due to some other cause. Series C showed that the lime and silica required increased as the lower ratio 5.44 disintegrated and the higher ratios were good. To sum this up, when all iron is used the  $\text{R}_2\text{O}_3 : \text{SiO}_2$  ratio should be below 5.1; when 0.175 to 0.2 mols.  $\text{Al}_2\text{O}_3$  is used with 0.825 to 0.8 mols. of  $\text{Fe}_2\text{O}_3$  the ratios lie between 5.1 to 7.22. If 0.36 to 0.4 mols. of  $\text{Al}_2\text{O}_3$  the ratio must be 5.8 or greater. This is but a suggestion and will require further experimenting to show it definitely.

2. That cements with large amounts of  $\text{Fe}_2\text{O}_3$  will stand saline solutions better than cements containing  $\text{Al}_2\text{O}_3$  was shown in the test of Series C where the Portlands were actually disintegrated and the iron cements stood the same test.

3. The results seem to suggest that if the amount of lime was reduced lower than 2.8 CaO in Bleininger's formula, better strength could be obtained. There was found in the bottom of the vessel, after each trial in the cylinder, a heavy muddy deposit which was principally hydrated lime and which appeared to have been leached from the cubes. This reduction of the amount of lime may not need to be as much as the results suggest if the raw materials were clay and limestone in place of pure whiting,  $\text{Al}_2(\text{OH})_6$  and flint. All of the iron cements would have stood the tests better if they had been allowed to stand in the atmosphere and age, thus giving the lime time to become calcium carbonate. The Portland cement, which these cements were tested against, was one of the best cements on the market. It tested as follows: Initial set, 3 hr.; final set  $4\frac{1}{2}$  hr.; tensile strength of neat cement after seven days, 679 lb.; after 28 days, 774 lb.; and its crushing strength is shown in the tables. This cement had also aged several months in the laboratory and was in the best of condition



to stand accelerated tests. The percent of lime given by Mr. William Michaelis is 63.5 per cent with a small amount of magnesia, MgO, 1.5 per cent. The cements made for this thesis are all above 66 per cent, this is only another evidence that these conclusions are correct and the following formula is suggested as the center of a series of cements for further experimenting:



from this vary both the amount of  $\text{SiO}_2$  and CaO.

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## BULLETIN No. 20

DEPARTMENT OF CERAMICS

R. T. STULL, Acting Director

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## DESIGNS OF SEVEN TEST KILNS

BY

R. T. STULL AND R. K. HURSH

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1913-1914



## DESIGNS OF SEVEN TEST KILNS

BY R. T. STULL AND R. K. HURSH, URBANA, ILLINOIS

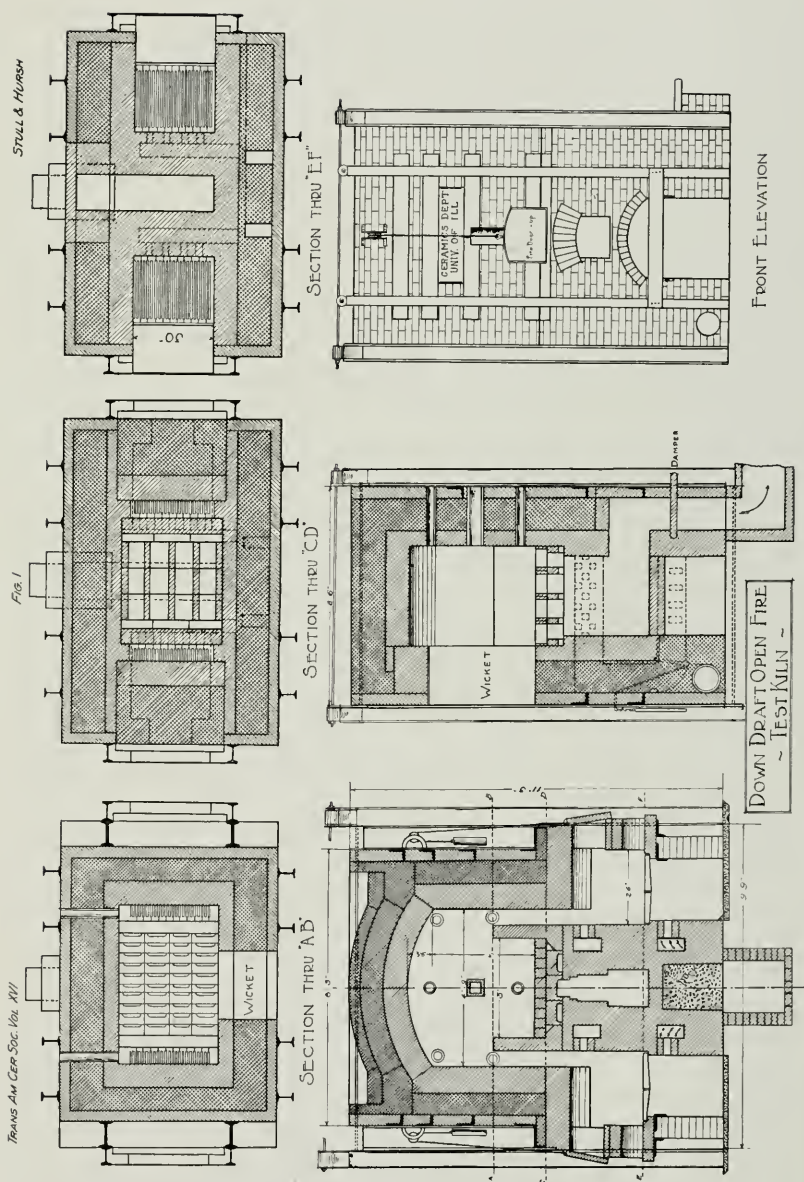
In presenting the designs of these test kilns, no claims are made to original ideas. In the design of each kiln, an attempt has been made to combine well-known principles in such a manner as to best meet the conditions and requirements which the kiln is to meet.

All flues leading from the kilns are placed under the floor. These connect with two main flues 15 in. wide by 30 in. deep, which in turn connect with a 60 ft. stack. Kiln represented by Figs. 1 and 2 is of the down-draft, open fire type, provided with two fire boxes. The fire boxes are short and wide, facilitating easy cleaning and prolonged life of grate bars. The kiln is provided with a flue system so that forced draft may be applied either above or below the grates. The kiln has been in use over two years and has been fired repeatedly to cone 16. It has a surplus of draft so that it has not been necessary to use forced draft to reach high temperatures.

In Figs. 3 and 4 is shown a rectangular down-draft muffle kiln. The muffle is 2 ft. by 3 ft. and 3 ft. to the spring. The muffle walls are laid with hollow blocks beveled at the corners in order to give greater radiation surface. The same size and style of fire box is used in this kiln as in the former one. The kiln has been burned to cone 8 in twelve hours. After two years of use, it is in excellent condition.

Figures 5 and 6 represent a round down-draft open fire kiln. Fuel oil, delivered to the kiln under 5 lbs. pressure, and air at 2 lbs. are used in firing. The four burners lead tangentially into a combustion ring. The fire gases pass up over a circular flash wall and down through the perforated floor.

The crown is removable and is raised and lowered by a three ton chain hoist running on a track. This arrangement permits of easy and quick setting and eliminates the troublesome cold doorway. The temperature and kiln atmosphere can be governed very closely. The kiln has been in use for more than a



year. Although it is capable of attaining very high temperatures, there has been no occasion to fire it above cone 8. This temperature has been attained with only two burners in use.

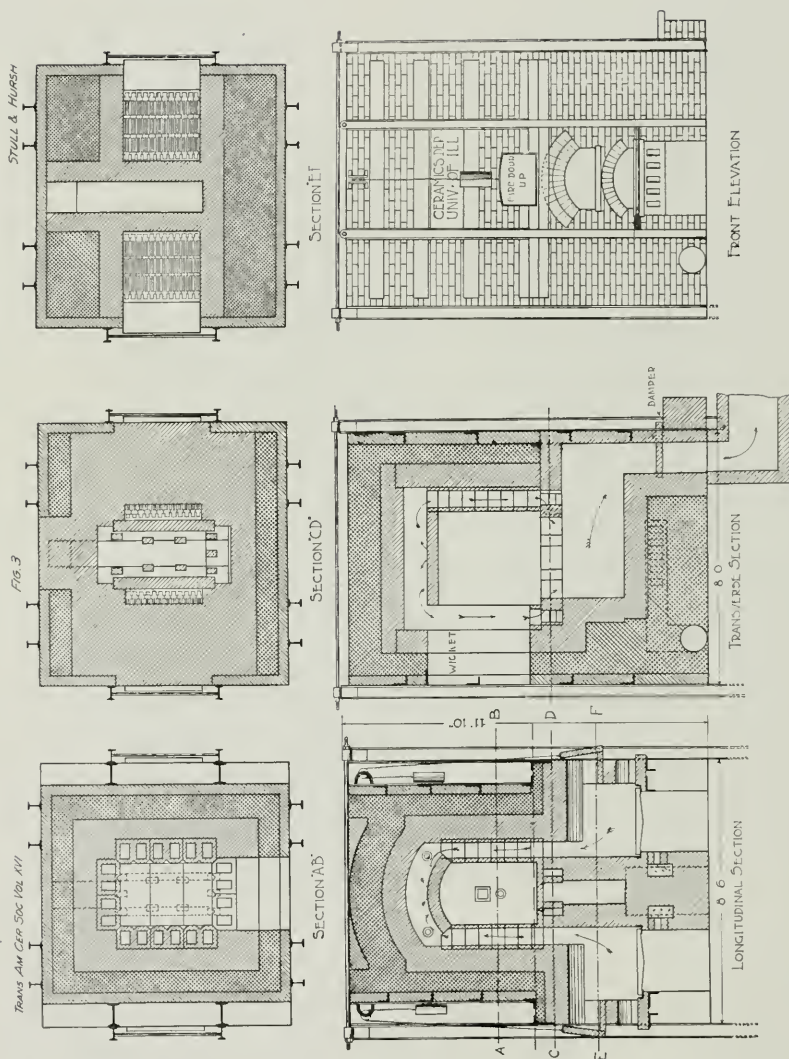
Figures 7 and 8: Open fire, down-draft kiln: The kiln is fired by gas and compressed air, both being preheated in coils



FIG. 2

of wrought iron pipe suspended in the out-going flue. The flue is provided with an opening just below the damper. Through this, air can be admitted in order to prevent over-heating of the coils. The kiln is fired by ten burners made from ordinary pipe fittings. Each burner is about the size of an ordinary Bunsen blast lamp. The kiln has been fired to cone 14 in six hours.







The setting chamber is 12 in. by 22 in. by 9 in. to the spring, and 4 in. rise. The kiln is especially adapted to clay testing. Two plugs in the crown, one in the back and one in the wicket, are provided for drawing trials.

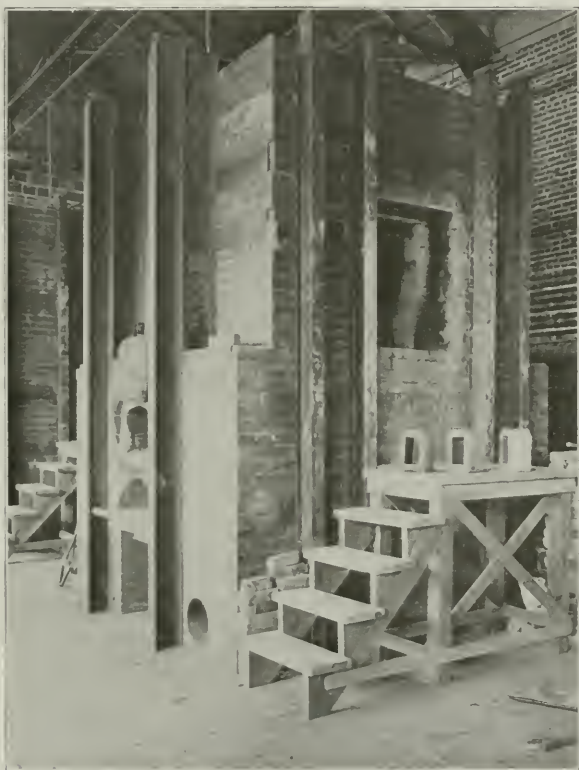


FIG. 4

Figure 9: Battery of three calcining kilns: Each unit is fired by fuel oil and compressed air. The combustion chamber at the top is cylindrical in form, the flame entering tangentially. Each unit is provided with two calcining chambers. The kilns are designed especially for burning small batches of Portland cement, and for calcining clays and dry colors. The material

to be calcined may be placed on the bottom plate of the chamber or in covered flat tile saggars.

Figure 10: Twin muffle kiln: The kiln was designed especially for firing enamels for metals and overglaze colors. Each muffle is heated by two gas burners, the air being preheated in the recuperator below the muffle. The gas passes in horizontally and meets the air coming up from the recuperator. The flame passes back to the opposite end of the muffle then turns and passes twice around the muffle to the center and down into the recuperator. The hottest parts of the flames from the two burners applied to each muffle, moving in opposite directions, encircle the muffle ends first, then encircle the middle, thereby neutralizing the "cold end" effect and giving a more uniform muffle temperature.

Figure 11: Battery of four drop-frit furnaces: Each furnace is fired by two small gas burners made from pipe fittings. The gas and air are preheated in wrought iron pipe coils placed in the outgoing flue. The flames pass into the combustion ring tangentially, then pass over a flash ring and down around the crucible. The frit pan underneath when filled with water forms a "water seal." The bottom of the pan is curved so that the frit can be raked out, making it unnecessary to remove the pan. The principal objection in the construction of the furnace is that the frit pan is too close to the fire. It should be placed about two to three courses of brick lower in order to obviate the rapid evaporation of the water and the burning of the top of the pan.

Ceramic Laboratories,  
University of Illinois

## DISCUSSION

*Mr. Blair:* Will Professor Stull give us an idea of the cost of ~~burning~~ that first kiln?

*Prof. Stull:* Yes I can give you an idea of the cost. Like Professor Bleininger, I did not want to scare you to death with the figures. A large fill was made on the present site of the new kiln house. In building the foundations for these kilns, it was necessary to go down so deep to get solid ground that it brought

up the costs enormously. The cost of that part below ground is nearly as much as that above ground. The first furnace shown cost between seven hundred and eight hundred dollars, that is, as near as I can remember. The figure given is for the kiln complete, including foundation, flues, iron work and all. Plenty of iron work has been placed on all kilns with a view to having them well braced.

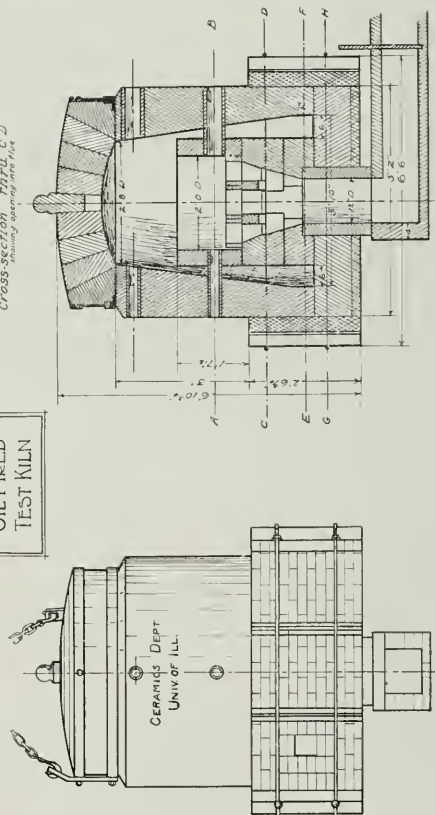
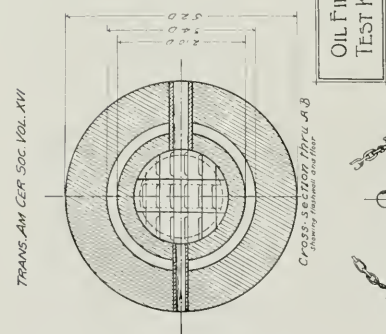
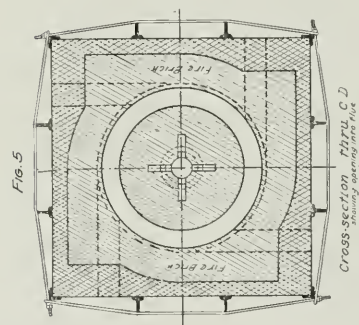
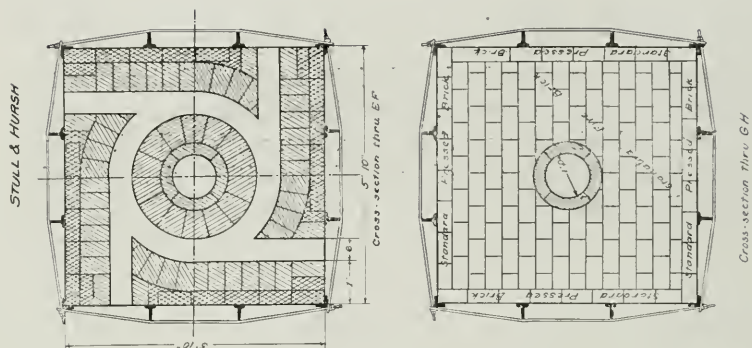




FIG. 6



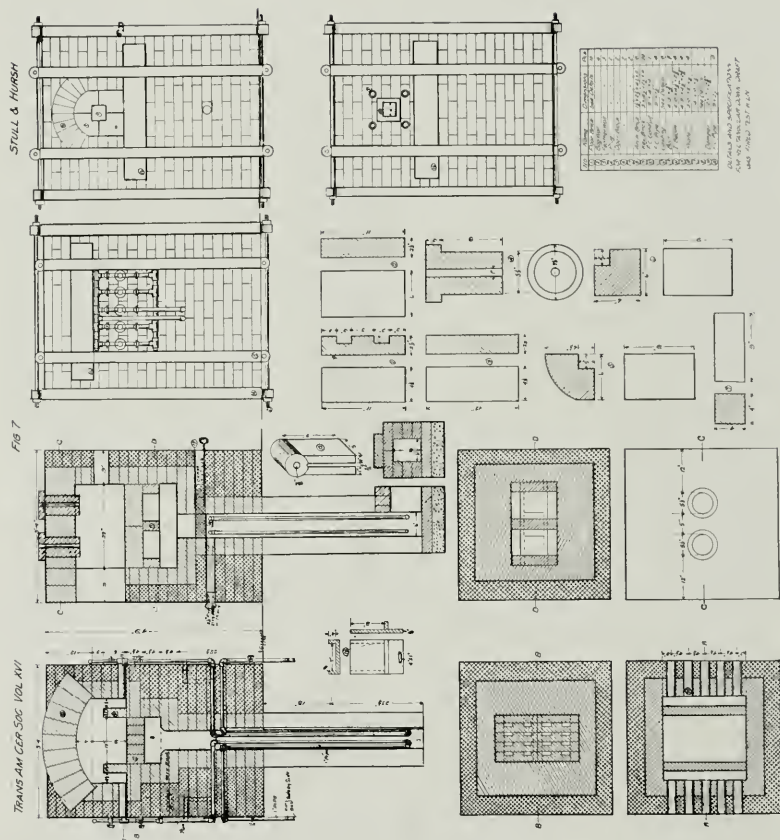


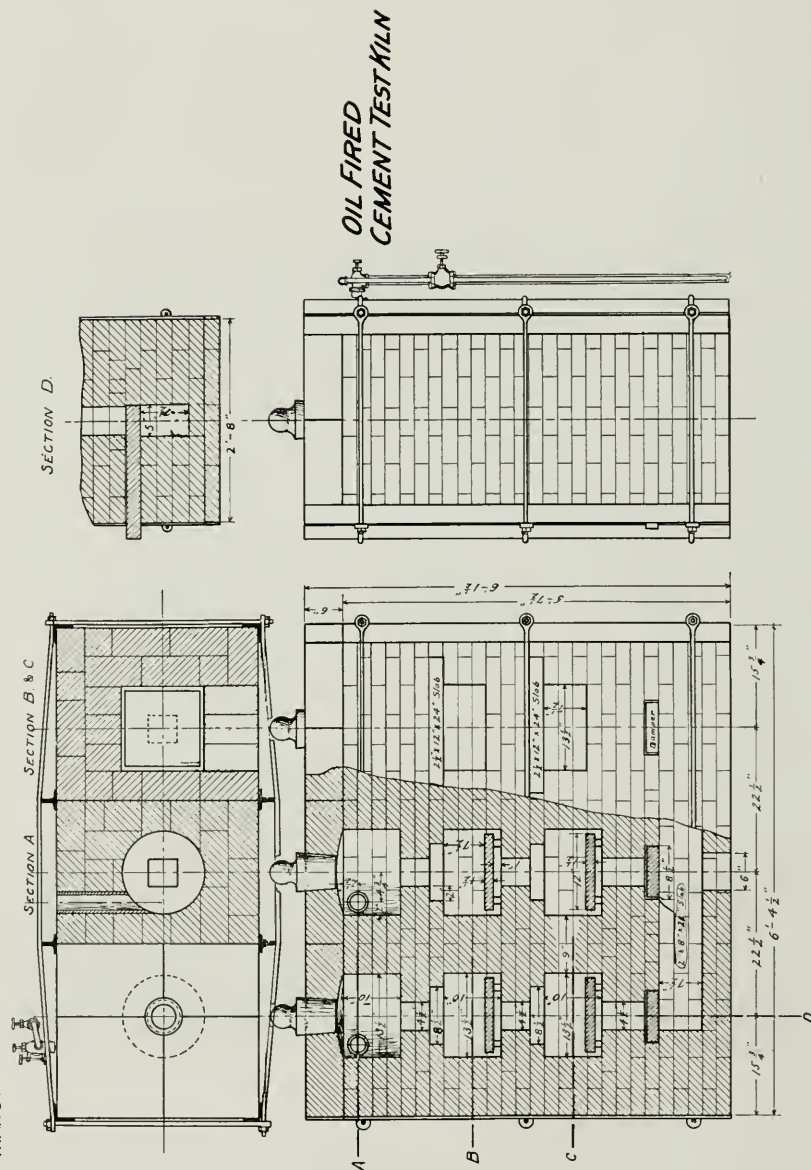


FIG. 8



FIG. 9.

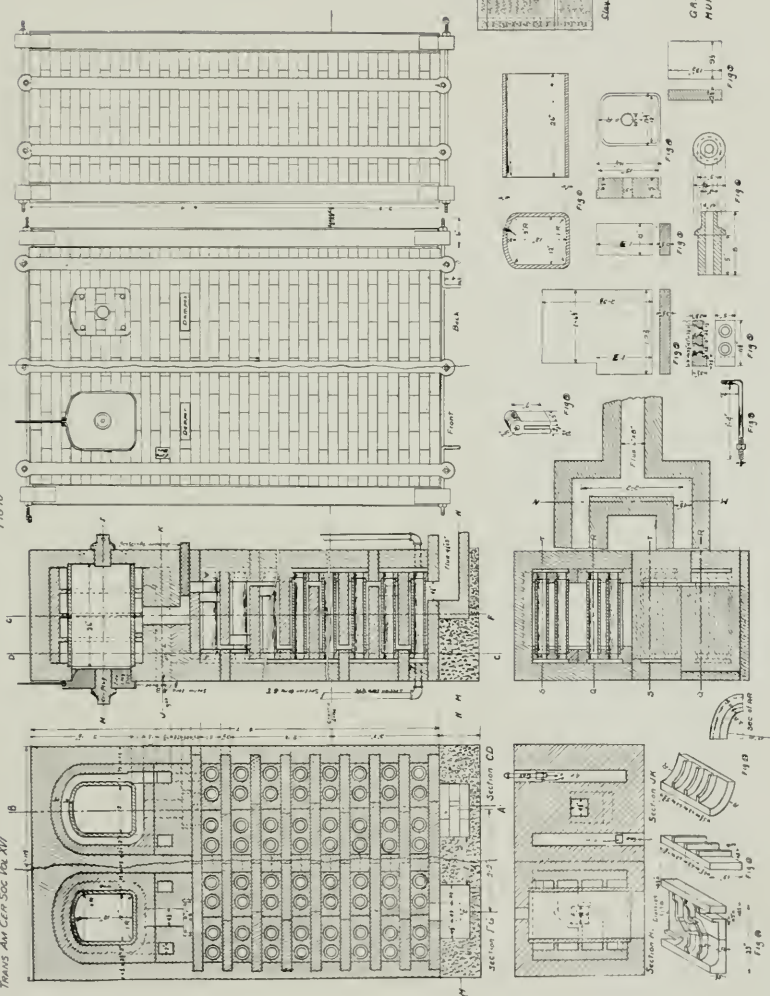
TRANS. AM. CER. SOC. VOL. XVI



STOLL &amp; HUMPH

FIG. 10

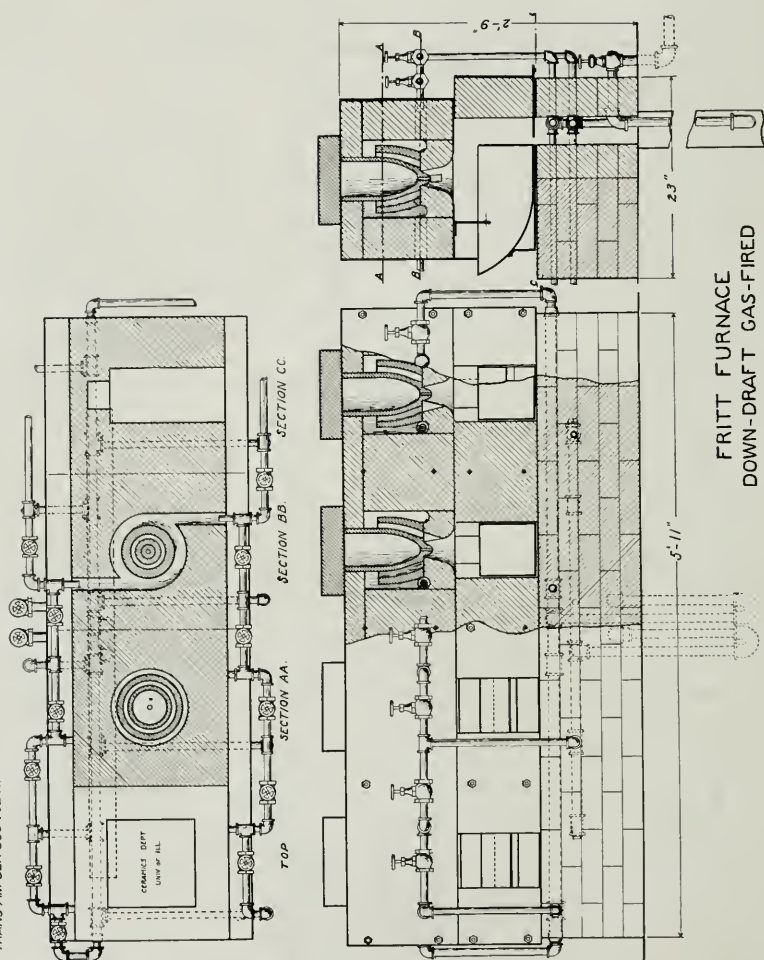
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STULL &amp; HURSH

TRANS AM CER SOC VOL XVII

FIG. 11.



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# UNIVERSITY OF ILLINOIS BULLETIN

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JULY 6, 1914.

No. 45

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## BULLETIN No. 21

DEPARTMENT OF CERAMICS

R. T. STULL, Acting Director

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### DEFORMATION TEMPERATURES OF SOME PORCELAIN GLAZES

BY

R. T. STULL AND W. L. HOWAT

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### A TYPE OF CRYSTALLINE GLAZE AT CONE 3

BY

C. C. RAND AND H. G. SCHURECHT

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PUBLISHED BY THE UNIVERSITY OF ILLINOIS, URBANA

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## DEFORMATION TEMPERATURES OF SOME PORCELAIN GLAZES

R. T. STULL AND W. L. HOWAT, URBANA, ILL.

The group of glazes studied comprises ten horizontal series designated by letters from A to J, each series consisting of ten members. The group of one hundred members covers the following limits represented by the four corner glazes:

TABLE I—FORMULA OF CORNER GLAZES

GLAZE	K <sub>2</sub> O	CaO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>
A-1 .....	0.3	0.7	0.40	2.0
A-10 .....	0.3	0.7	0.40	6.5
J-1 .....	0.3	0.7	0.85	2.0
J-10 .....	0.3	0.7	0.85	6.5

TABLE II—BATCH WEIGHTS

	BRANDY- WINE FELDSPAR	WHITING	ENG. NO. 20 BALL CLAY	N. C. KAOLIN	FLINT	Al <sub>2</sub> (OH) <sub>3</sub>
A-1 .....	167.4	70.0	12.9	12.9	.....	....
A-10 .....	167.4	70.0	12.9	12.9	270.0	....
J-1 .....	167.4	70.0	12.9	12.9	.....	70.2
J-10 .....	167.4	70.0	70.9	70.9	216.0	....

Different members in the group were made by molecular blending of the four extremes. These were applied to bisque wall tile, set in saggars in a down draft kiln and burned to cone 9 in 40 hours.

Cones were also made from the glazes and their deformation temperatures determined in a platinum resistance furnace, the temperatures being measured by a platinum, platinum-rhodium thermocouple and a Leeds-Northrup direct reading potentiometer, (accurate to 3°C).

The time-temperature curve followed in all determinations is shown in Figure 1. The temperature was raised to  $1200^{\circ}\text{C}.$  in 120 minutes. Beyond this the temperature rise was  $2\frac{1}{2}$  degrees per minute. A number of deformation tests made on duplicate Seger cones gave the following results: cone 4— $1212^{\circ}\text{C}.$ , cone 6— $1255^{\circ}\text{C}.$ , cone 8— $1290^{\circ}\text{C}.$

Deformation-temperature readings were made on two or more cones of each glaze. The variation was rarely over  $5^{\circ}\text{C}.$ , and in the majority of tests, duplicate cones gave the same temperature readings.

TABLE III—DEFORMATION TEMPERATURES COVERING THE LIMITS

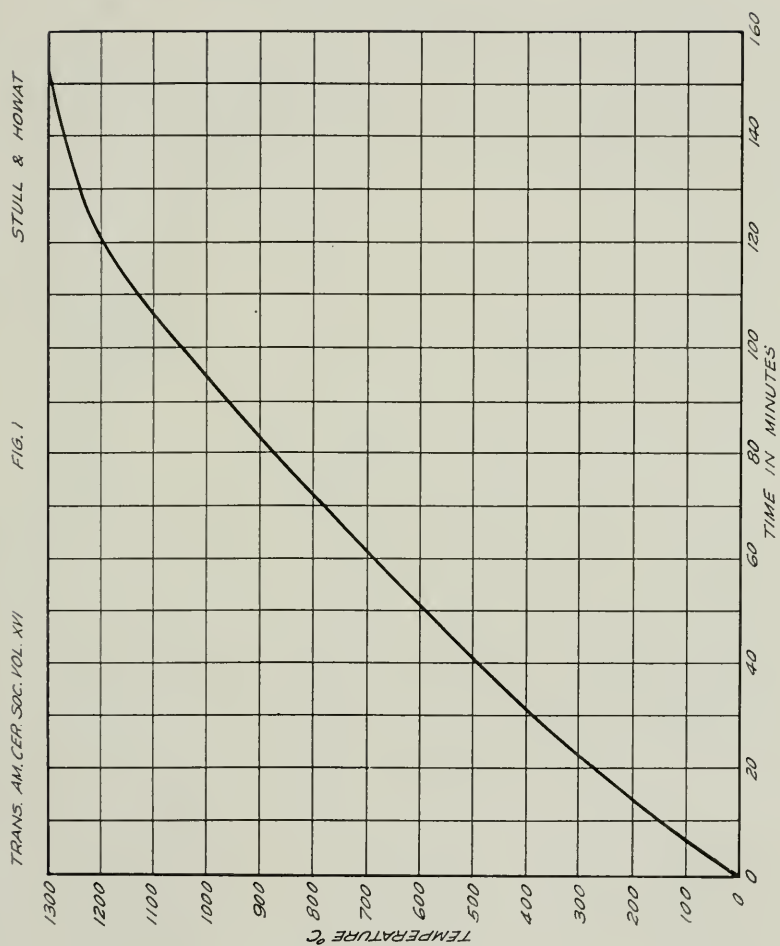
$$\begin{array}{l} 0.3 \text{ K}_2\text{O} \\ 0.7 \text{ CaO} \end{array} \left\{ \begin{array}{l} 0.40 \text{ to } 0.85 \text{ Al}_2\text{O}_3 : \\ 2.0 \text{ to } 6.5 \text{ SiO}_2 \end{array} \right.$$

	1	2	3	4	5	6	7	8	9	10	MOL. CULES Al <sub>2</sub> O <sub>3</sub>
J	1277	1246	1232	1235	1247	1252	1248	1260	1267	1265	0.85
I	1275	1240	1228	1230	1240	1235	1245	1247	1250	1252	0.80
H	1272	1245	1232	1230	1230	1232	1235	1235	1245	1245	0.75
G	1272	1240	1228	1228	1232	1232	1233	1237	1235	1247	0.70
F	1267	1238	1225	1225	1225	1225	1228	1235	1235	1245	0.65
E	1232	1225	1225	1222	1220	1225	1228	1235	1245	1245	0.60
D	1230	1225	1225	1227	1230	1230	1240	1245	1248	1252	0.55
C	1232	1228	1228	1228	1228	1230	1240	1248	1252	1255	0.50
B	1235	1230	1228	1233	1235	1245	1254	1252	1257	1270	0.45
A	1232	1232	1240	1245	1245	1255	1255	1268	1272	1277	0.40
MOL. CULES SiO <sub>2</sub>	2.0	2.5	3.0	3.5	4.0	4.5	5.0	5.5	6.0	6.5	

The average temperature readings for two or more cones of each glaze of the group are given in Table III. The results of the burn and the iso-deformation lines are represented graphically in Figure 2, the deformation-temperature being indicated in degrees centigrade on each line.

The RO is constant for all glazes. The molecular variations of SiO<sub>2</sub> are plotted along the abscissa and the molecular variations of Al<sub>2</sub>O<sub>3</sub> on the ordinate.





In the lower right corner are the devitrified glazes between the limits:

RO, 0.4  $\text{Al}_2\text{O}_3$ , 5.0  $\text{SiO}_2$

RO, 0.4  $\text{Al}_2\text{O}_3$ , 6.5  $\text{SiO}_2$

RO, 0.6  $\text{Al}_2\text{O}_3$ , 6.5  $\text{SiO}_2$

In the lower portion of the devitrified area the glazes were crazed. In the center of the field are the bright glazes which were considered matured. Bright glazes which were crazed are found in the lower left corner within the limits:

RO, 0.4  $\text{Al}_2\text{O}_3$ , 2.5  $\text{SiO}_2$

RO, 0.4  $\text{Al}_2\text{O}_3$ , 2.0  $\text{SiO}_2$

RO, 0.5  $\text{Al}_2\text{O}_3$ , 2.0  $\text{SiO}_2$

At the left of the field a small group of matured mats are found between limits:

RO, 0.55  $\text{Al}_2\text{O}_3$ , 2.0  $\text{SiO}_2$

RO, 0.70  $\text{Al}_2\text{O}_3$ , 2.0  $\text{SiO}_2$

RO, 0.65  $\text{Al}_2\text{O}_3$ , 2.5  $\text{SiO}_2$

In the upper part of the field the glazes were under fired.

The difference between max and min deformation temperatures is  $57^\circ\text{C}$ ., the softest one deforming at  $1220^\circ\text{C}$ . having the formula, RO, 0.6  $\text{Al}_2\text{O}_3$ , 4.0  $\text{SiO}_2$ . The member at the upper left corner (RO, 0.85  $\text{Al}_2\text{O}_3$ , 2.0  $\text{SiO}_2$ ) and the one at the lower right corner (RO, 0.4  $\text{Al}_2\text{O}_3$ , 6.5  $\text{SiO}_2$ ) deformed at the max temperature  $1277^\circ\text{C}$ .

Each horizontal series may be considered as being composed of the components, glaze and  $\text{SiO}_2$ . The broken line CD passes through the deformation-eutectic of each of the ten glaze— $\text{SiO}_2$  series. In a vertical direction, consider each series made up of glaze and  $\text{Al}_2\text{O}_3$ , the dotted line EF represents the deformation-eutectic axis of the ten glaze— $\text{Al}_2\text{O}_3$  series.

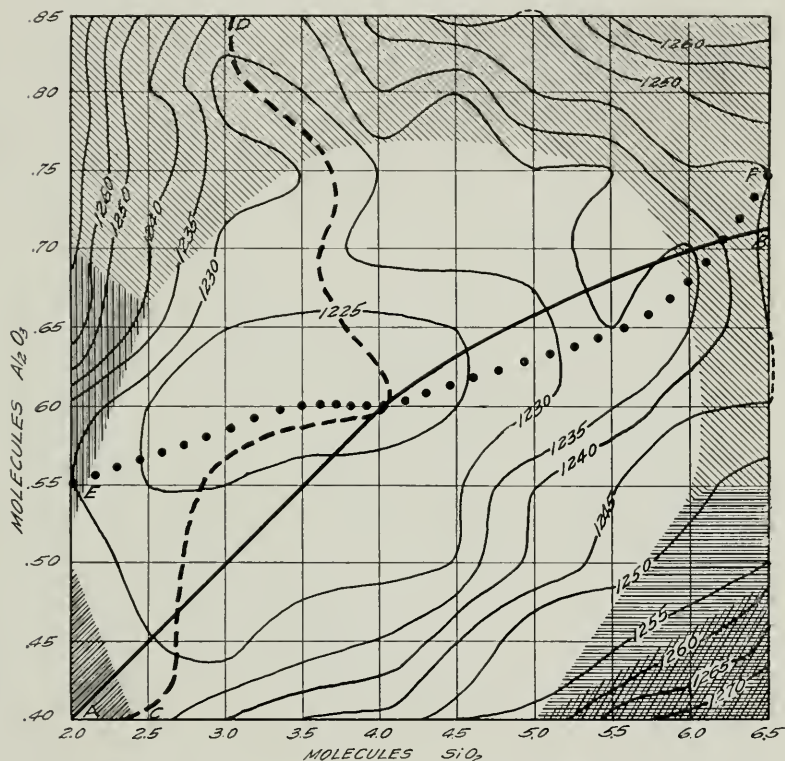
These two axes (CD and EF) cross at the point of lowest deformation temperature (group eutectic). Its deformation temperature is ten degrees higher than the indicated temperature of Seger cone 4. The glazes whose formulae correspond to cones 4, 5 and 6 deformed at  $1228^\circ\text{C}$ ,  $1240^\circ\text{C}$  and  $1245^\circ\text{C}$  respectively.

The line AB is the high gloss axis plotted according to the appearance of the glazed trials. The gloss axis follows roughly parallel to the glaze-SiO<sub>2</sub>, deformation-eutectic axis up to the group eutectic. Beyond this point it deflects and follows along

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FIG. 2

STULL &amp; HOWAT



CONE NINE BURN

 CONSTANT {
   
 .3 K<sub>2</sub>O
   
 .7 CaO

BRIGHT

MATT

IMMATURE

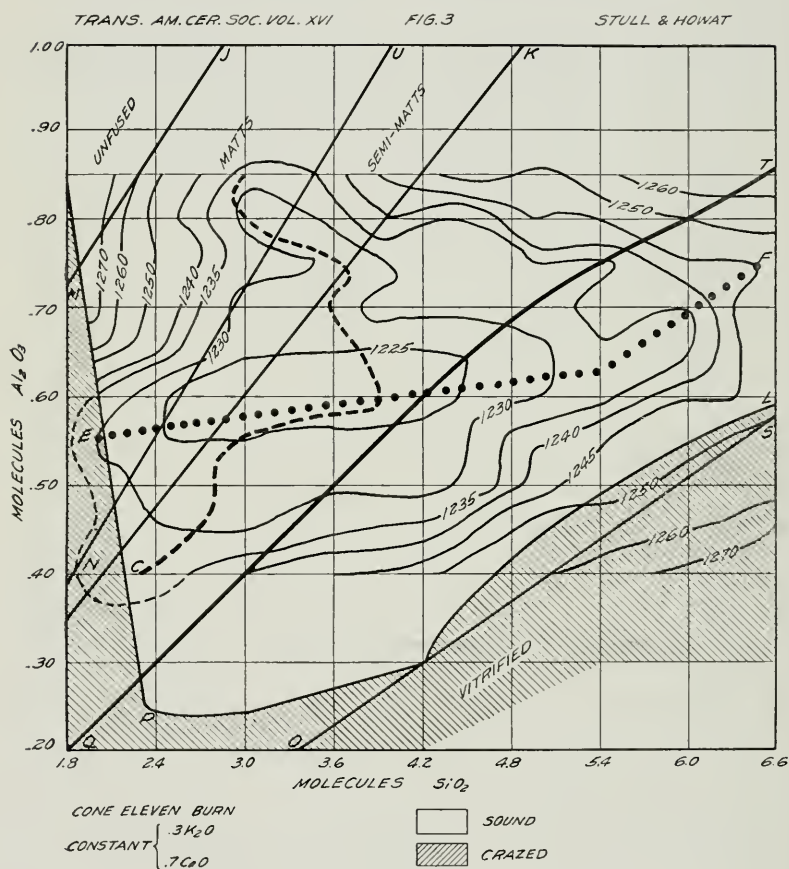
DEVITRIFIED

CRAZED

DEVITRIFIED CRAZED

the glaze-Al<sub>2</sub>O<sub>3</sub> deformation-eutectic axis. The group deformation-eutectic lies near the center of the field of best glazes, and the quality of the glazes decreases in all direction away from this eutectic point. The general formulae of the best glazes as shown by the trials are:

RO-0.60 $\text{Al}_2\text{O}_3$	4.0 $\text{SiO}_2$	Deformation temp. = 1220°C.
RO-0.55 $\text{Al}_2\text{O}_3$	3.5 $\text{SiO}_2$	Deformation temp. = 1227°C.
RO-0.55 $\text{Al}_2\text{O}_3$	4.0 $\text{SiO}_2$	Deformation temp. = 1230°C.
RO-0.60 $\text{Al}_2\text{O}_3$	3.5 $\text{SiO}_2$	Deformation temp. = 1222°C.



The difference between the deformation-temperatures of these glazes and the temperature to which they were fired (cone 9) is 80°C to 90°C, or a difference of 4 to 4½ cones. For the purpose of comparison the iso-deformation temperature lines are plotted on the field of porcelain glazes burned at cone 11 and

previously reported,<sup>1</sup> Figure 3. The high gloss axis QT lies to the right of the glaze-SiO<sub>2</sub> eutectic axis and crosses the glaze-Al<sub>2</sub>O<sub>3</sub> eutectic axis close to the eutectic member of the group. The best glazes in this group are found in close proximity to the group eutectic, the same as in the cone 9 burn. Not only does the group eutectic lie near the center of the area of best glazes, but it is also located at a safe distance away from devitrification, crazing, mattness and immaturity.

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University of Illinois.

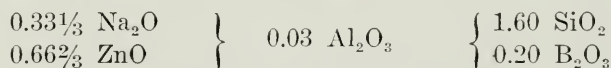
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<sup>1</sup> Influences of variable Silica and Alumina on Porcelain Glazes of Constant RO, *Trans. Amer. Cer. Soc.*, Vol. xiv, pp. 62-70.

## A TYPE OF CRYSTALLINE GLAZE AT CONE 3

C. C. RAND AND H. G. SCHURECHT, URBANA, ILL.

The glazes under consideration are of a type designed to mature about cone 3 to 4. The  $\text{Al}_2\text{O}_3$  is maintained constant throughout at .05 equivalent and is introduced as Pikes No. 20 English ball clay. In general the group resembles Worcester's<sup>1</sup> best raw clay glaze. His formula was



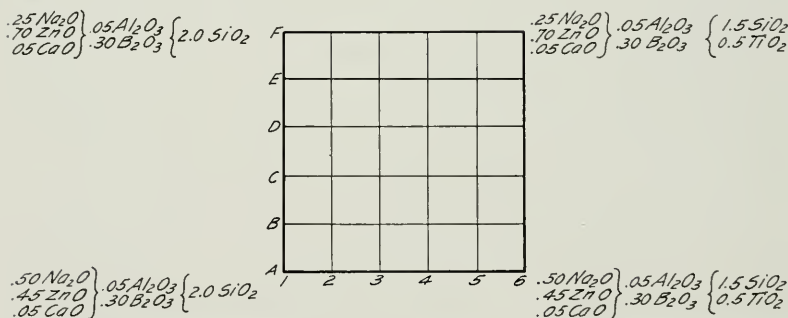
He concludes, however, that .05  $\text{Al}_2\text{O}_3$  generally seems the most favorable and that many German formulæ call for this amount.

A group of 36 glazes was made with a view to determine the effect of varying  $\text{ZnO}$  against  $\text{Na}_2\text{O}$  along the ordinate, and rutile against flint along the abscissa.

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FIG. 1

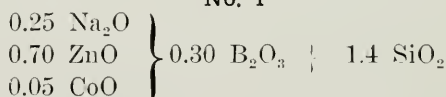
RAND & Schurecht



The arrangement of the group with the formulæ of the four corners are shown in Fig. 1, the vertical series being designated by numbers, the horizontal series by letters.

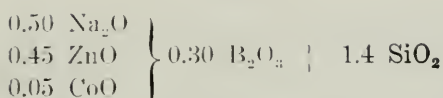
Two frits of the following compositions were used:

No. 1



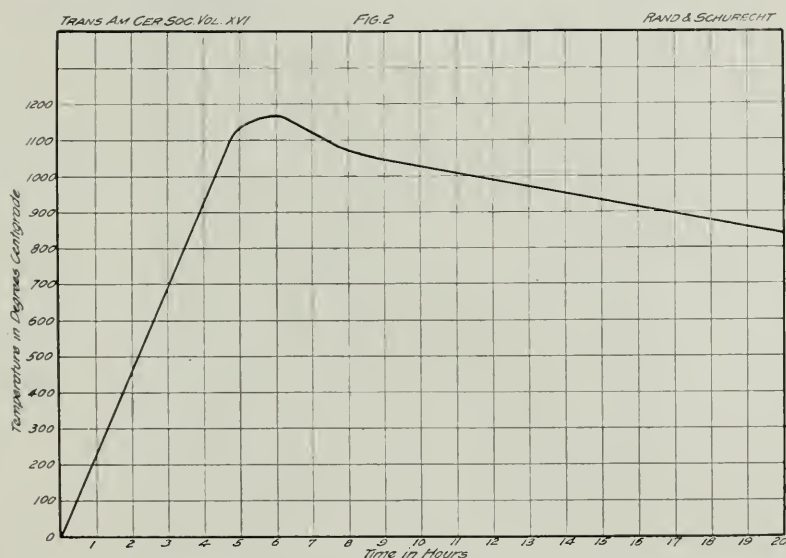
<sup>1</sup> Vol. X Trans. Amer. Cer. Soc., p. 150. Function of Alumina in Crystalline Glaze.

## No. 2



These were each intimately mixed and ground in small ball mills, fused, quenched in water, dried and ground to pass 80 mesh sieve.

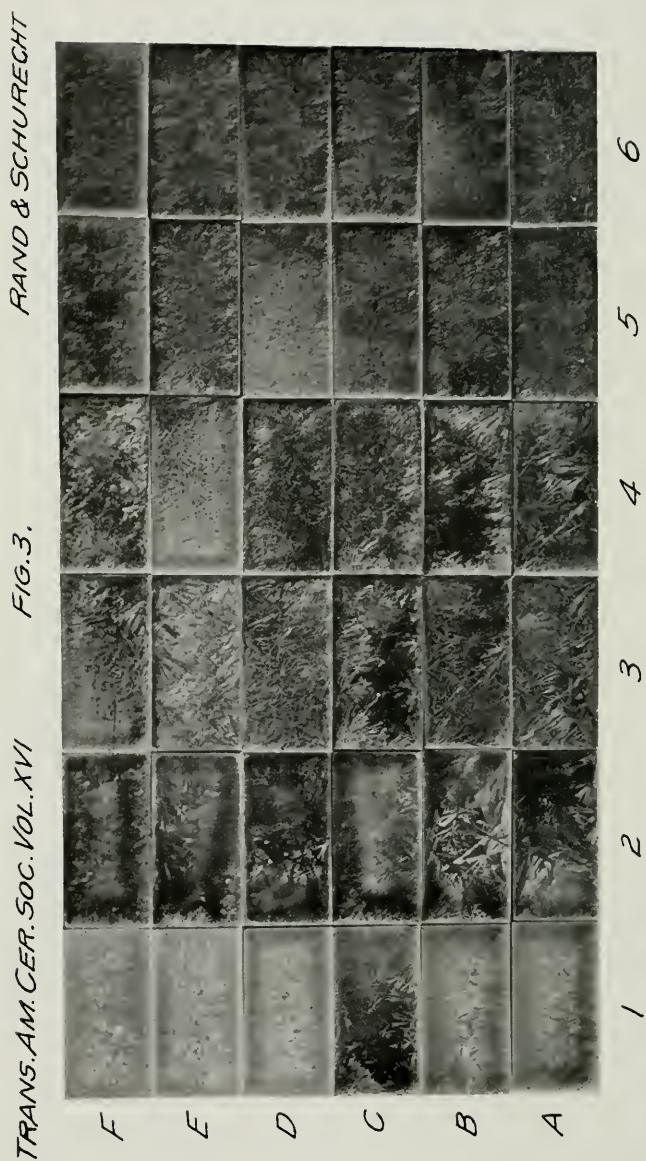
The four corner glazes were ground wet until they passed 120 mesh sieve, and the remaining glazes blended from them in molecular proportions.



The glazes were applied to two sets of biscuit tile by dipping, and burned to cone 3 in 5 hours in a round, down-draft, open-fired oil kiln. The fires were put out when the finishing temperature was reached and the kiln allowed to cool with the damper closed.

The results were not satisfactory, as only a few crystalline patches appeared. These patches increased noticeably as the content of ZnO increased. High ZnO also appeared to give a deeper blue as would be expected. E 3 showed the most crystallization.





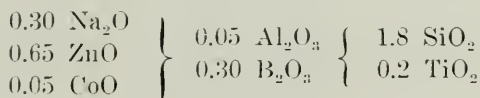
The failure to obtain good results was attributed to too rapid cooling, too thin coating of the glaze, and perhaps slight under burning.

Next two sets of trials were dipped, care being taken to obtain a thick coating of the glaze, and burned in the same kiln to cone 4, following the heating and cooling curve shown in Figure 2. The pyrometer showed a temperature of  $1170^{\circ}\text{C}$ , when cone 4 went down.

From a crystallization standpoint, the results, Fig. 3, were highly satisfactory. Every glaze showed a large number of crystals and in many cases was a solid mass of crystals of varying sizes. The variation of  $\text{ZnO}$  and  $\text{Na}_2\text{O}$  seems to have little, if any, effect upon either crystallization or color.

Increase in  $\text{TiO}_2$  has a marked effect upon both. As  $\text{TiO}_2$  increased the crystals became smaller, and more numerous, most of the high rutile glazes consisting of a mass of small interlocking crystals. At 0.0  $\text{TiO}_2$  and at 0.1  $\text{TiO}_2$ , a good blue color is shown, but from 0.1  $\text{TiO}_2$  up, the blue is partially and in some cases almost totally absent. Bronze patches are quite prominent, due possibly to iron impurities in the rutile.

The two sets of trials are very nearly identical. Glaze E 3, with the formula

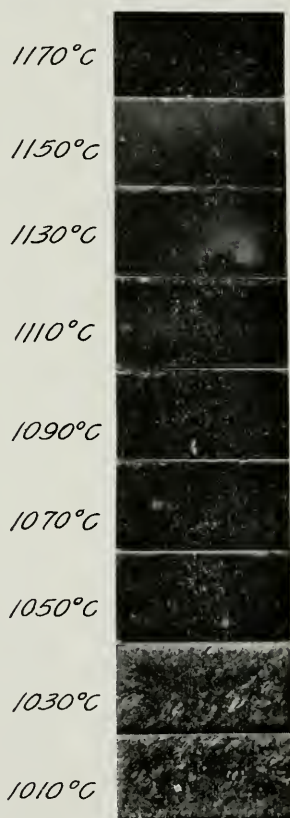


again appears to contain the most crystals and for this reason was selected as the glaze to use in making draw trials with a view to noting different stages of crystallization.

The glazes were dipped and burned in the same manner as before, a number of trials of E 3 being placed where they could be drawn. One was drawn at the finishing point, and one every  $20^{\circ}$  as the cooling progressed. The third trial drawn showed crystals around the edges. The amount of crystallization increased steadily for four trials. The next trial at  $1030^{\circ}\text{C}$  showed a very great increase, the glaze consisting of a mass of crystals. It is possible that this is due to the crystallization of an eutectic.

That is, the compound forming the crystals shown first continued crystallizing out until the melt reached the composition of the eutectic mixture, when the whole mass crystallized. (Fig. 4.)

*TRANS. AM. CER. SOC. VOL. XVI FIG. 4. RAND & SCHURECHT*



One set of trials was placed on edge in this last burn. They failed to show as much crystallization as those lying down, as the glaze had run off to a great extent. However, good results were obtained on two small vases to which the glaze had been applied in a very thick coat, though here also, much of the glaze had been lost.

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BULLETIN No. 22

DEPARTMENT OF CERAMICS

R. T. STULL, Acting Director

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THE INFLUENCE OF CHLORIDES OF CAL-  
CIUM AND IRON WHEN PRECIPITATED  
IN A PORCELAIN BODY

---

SOME COBALT-URANIUM COLORS

BY

B. S. RADCLIFFE

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PUBLISHED BY THE UNIVERSITY OF ILLINOIS, URBANA

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1913-1914



## THE INFLUENCES OF CALCIUM AND IRON CHLORIDES PRECIPITATED IN A PORCELAIN BODY

BY B. S. RADCLIFFE

The production of vitrified red floor tile has given manufacturers considerable trouble. Practically, the only solution of the problem has been to secure a good red burning clay, and burn to a degree of vitrification such that the red color is not destroyed. In most instances, it has been found impossible to make red bodies that have less than four or five percent absorption, and in many cases the absorption is considerably greater than this.

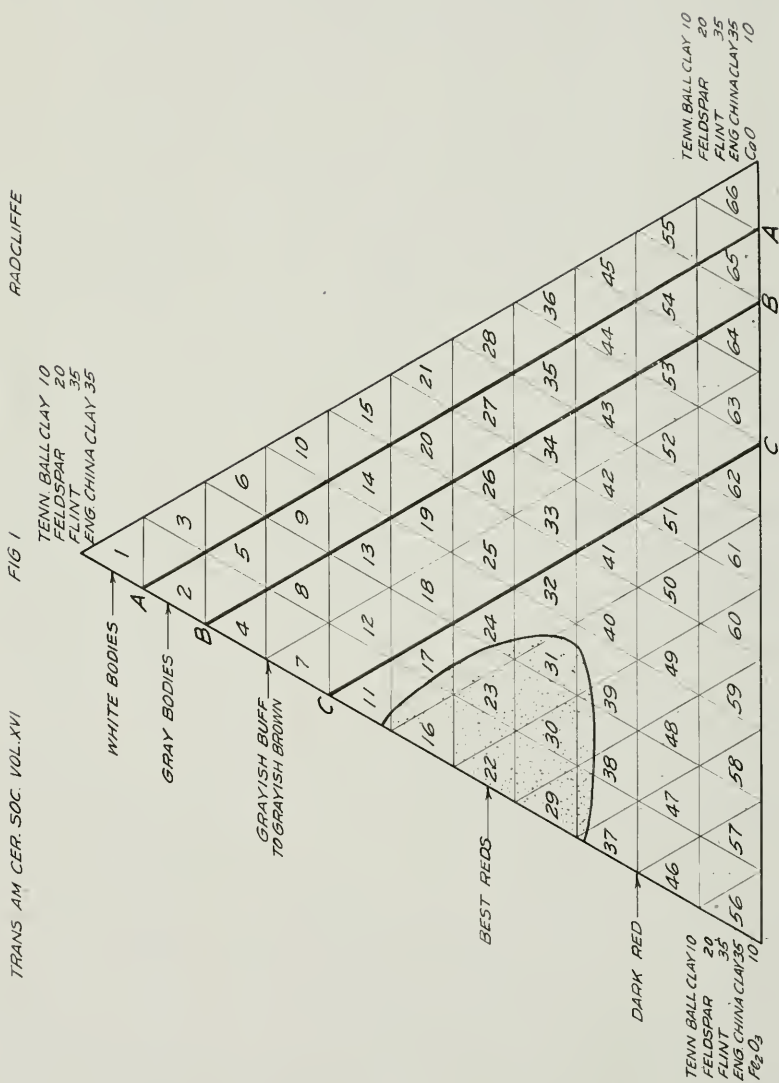
Good red bodies can be made by mixing the proper amounts of feldspar and flint with "Helmstadter" clay, and burning to practically complete vitrification.

This clay is very fine grained, plastic, and is red in color. The original red color of the clay is only slightly altered during burning, up to the point when the porosity is reduced to about three percent. A higher temperature causes the red color to deepen and gradually change to dark brown and finally black. The deepening of the color begins about cone 6, and by cone 8 the body is dark brown to black. The burning qualities of this clay seem to be due to the fact that the iron is present in a highly disseminated state.

This investigation was made to determine whether uniform colors of iron in varying shades could be produced by precipitating the chlorides of iron and calcium in a body.

A cone 10 porcelain was chosen for the body. It is not considered an ideal one for the production of red tile, and one containing more ball clay in place of the china clay would probably be better, since it would have less porosity in the dry state and would require less fluxing action for complete vitrification on that account.

**Procedure.** The three corner bodies as shown on the tri-axial diagram were mixed by wet-grinding for five hours in a porcelain-lined ball-mill. The tri-axial group of 66 bodies was made by blending these three bodies.





The mixtures were put in fruit jars and shaken thoroughly so as to obtain uniform mixtures. The chlorides were precipitated by adding  $\text{NH}_4\text{OH}$  and  $(\text{NH}_4)_2\text{CO}_3$  and shaking. The slips were allowed to stand for a day, after which they were poured into plaster molds. When the excess water had been absorbed the bodies were removed from the molds, and dried in an oven to  $200^\circ\text{C}$ . After crushing in a porcelain mortar, triangular floor-tile were made by the dry-press process, about 10 percent of water being used. They were burned to cones 5, 7, 9 and 11 in an open, down-draft, gas-fired test kiln.

**Results.** Those bodies high in iron were most plastic, and those high in lime were least plastic. This was shown both by the working properties of the bodies in the plastic state and by the strength of the dried tile.

**Vitrification**—None of the bodies were completely vitrified at cone 5, although those high in iron and lime were hard and dense, those high in lime being the hardest. At cone 7, all bodies containing over four percent of fluxes were vitrified. All bodies were completely vitrified at cone 9, those containing over 7 percent of fluxes being overburned.

Bodies containing 4 percent and over of fluxes were overburned at cone 11. The remainder retained their shape but had a glassy surface with the exception of 1, 2 and 3.

**Color**—Bodies free from iron burned white and were practically uniform in color at vitrification.

Those containing 1 percent of iron were cream colored when burned under oxidizing conditions, but a good uniform gray color was obtained when the tile were reduced at the end of the burn. The lime had very little effect upon the color of bodies containing 1 percent of iron. Bodies containing 2 percent of iron were pink or light red at cone 5, above which temperature they changed to brownish buff with the exception of No. 4, which became dark yellowish gray.

Bodies containing 4 to 10 percent of iron burned red to dark red at cone 5. Those containing 4, 5 and 6 percent were still red at cone 7. The color was much deeper than at cone 5 and in-

creased with increased iron. Two percent of lime did not affect the color of bodies containing 5 percent or over of iron.

The remainder of the series did not produce desirable colors for floor tile.

### CONCLUSIONS

Uniform gray colors of pleasing shades can be made by precipitating 0 to 2 percent of iron in a porcelain body and burning properly.

Uniform red colors can be produced by precipitating 4 to 6 percent of iron in a porcelain body which, if burned properly, would not have more than 3 to 4 percent porosity.

Ceramic Laboratory,  
University of Illinois

### DISCUSSION

*Mr. Parmelee:* I should like to ask the reason for using calcium salt.

*Mr. Radcliffe:* Calcium chloride was added, because it is a soluble salt; and it was thought, that the intimate mixture of the calcium and iron obtained in this way, might throw some light on the cause of the varied color effect, produced by iron in different clays.

# SOME COBALT-URANIUM COLORS

BY B. S. RADCLIFFE

There are four coloring oxides, namely, copper, chromium, nickel and iron, which under proper conditions produce green colors in bodies and glazes. In physical mixtures, we are able to produce greens by blending blue and yellow.

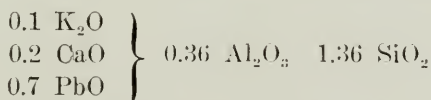
The object of this investigation was to determine whether green could be produced by blending cobalt-blue and uranium-yellow.

Series A was made up as follows:

TABLE I—SERIES A

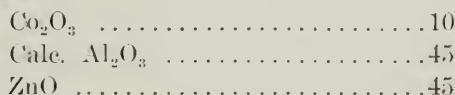
	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	A <sub>4</sub>	A <sub>5</sub>
Co <sub>2</sub> O <sub>3</sub> .....	1.0	0.9	0.8	0.7	0.6
Na <sub>2</sub> U <sub>2</sub> O <sub>7</sub> 6 H <sub>2</sub> O.....	50.0	50.0	50.0	50.0	50.0
Al <sub>2</sub> (OH) <sub>6</sub> .....	40.0	40.0	40.0	40.0	40.0
ZnO.....	25.0	25.0	25.0	25.0	25.0

The stains were thoroughly mixed, calcined to cone 5, ground to pass a 200 mesh screen and added to a mat glaze having the formula,



The glaze was then burned to cone 05. The result was a yellowish green glaze with blue specks. This was due to the fact that the cobalt was not thoroughly disseminated.

A blue stain



was then made, calcined to cone 7, and ground to pass a 200 mesh screen.

Three frits were made using the mat glaze as before.

## SOME COBALT-URANIUM COLORS

TABLE II—SERIES B

	B <sub>1</sub>	B <sub>2</sub>	B <sub>3</sub>
Feldspar.....	17.6	17.6	17.6
CaCO <sub>3</sub> .....	6.3	6.3	6.3
Red lead .....	50.5	50.5	50.5
Eng. china clay.....	11.0	11.0	11.0
Tenn. ball clay.....	10.0	10.0	10.0
Flint.....	4.6	4.6	4.6
Blue stain.....	10.0	10.0	10.0
Na <sub>2</sub> U <sub>2</sub> O <sub>7</sub> 6 H <sub>2</sub> O.....	25.0	25.0	45.0

When applied as glazes, B 1 gave an olive green, B 2 and B 3 rich chocolate browns. These results indicate that the ratio of uranium to cobalt is too high.

The next step tried was to use the nitrates of cobalt and uranium, by fritting in the mat glaze.

TABLE III—SERIES C

	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>
Feldspar.....	17.6	17.6	17.6
CaCO <sub>3</sub> .....	6.3	6.3	6.3
Red lead .....	50.5	50.5	50.5
Eng. china clay.....	11.0	11.0	11.0
Tenn. ball clay.....	10.0	10.0	10.0
Flint.....	4.6	4.6	4.6
Cobalt nitrate .....	3.5	3.5	3.5
Uranium nitrate.....	10.0	12.0	15.0

The frits were ground, and a series of glazes made by blending with the original mat glaze.

Bright glazes were made by adding 20 parts of flint to the frits of this series.

The mat glazes were olive green, C<sub>1</sub> having a bluish shade.

Of the bright glazes C<sub>3</sub> was deep green in color, and C<sub>1</sub> and C<sub>2</sub> were green with a bluish shade.

**Conclusions:** Green glazes and mats can be made by blending cobalt and uranium in the right proportions, which is between four and five parts of uranium nitrate to one part of cobalt nitrate.

Ceramic Laboratory,  
University of Illinois.

### DISCUSSION

*Prof. Orton:* I do not know, whether there has ever been any report made, about the peculiar green developed by one of the roofing-tile plants in this country by the use of cobalt oxide and sulphate of antimony. These coarsely ground chemicals were added to a roughly prepared glaze; and the result was that they succeeded in getting a very passable green. At least it looked like a good green on the roof, but if looked at close by, the size of the blue and yellow spots was so large as to be offensive. The reason, that they did this, was that they were working in a sulphurous close atmosphere, that spoiled other greens, and they thought, that if they had a sulphate to start with, it would not do any harm.

*Mr. Radcliffe:* I might say that a man in the terra-cotta business in Kansas told me that he used cobalt and uranium to produce greens. He did not tell me, however, until we worked it out. He was using it for polychrome work. The cobalt-uranium green that he produced was better than any other green that he could make for this purpose. It did not run or blend off with the white, but instead he could get a firm line between the green and the white, or whatever base was beneath the green polychrome work.



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## BULLETIN No. 23

DEPARTMENT OF CERAMICS

R. T. STULL, Acting Director

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### NOTES ON THE DEVELOPMENT OF THE RUBY COLOR IN GLASS

BY

A. E. WILLIAMS

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## NOTES ON THE DEVELOPMENT OF THE RUBY COLOR IN GLASS

BY A. E. WILLIAMS

The term "ruby glass" is applied to red glass colored by the use of copper, gold, selenium and in some cases, flowers of sulphur, the color varying considerably in intensity and shade. In case of copper, the color varies from amber to various shades of reds to brown and to opaque black. With gold the red has a rose tint, and selenium ruby seems to be a brighter red of varying intensities. The red from sulphur is rather unreliable, in that a uniform color is hard to obtain, and therefore only used for lower grades of glass.

Copper and gold reds are said to be due to the metals in suspension as colloids.

V. Pöschl<sup>1</sup> describes the preparation of Purple of Cassius from gold, and shows that the red or the purple gold-hydrosol may be obtained, depending upon the proper electrolyte present.

Paal's<sup>2</sup> process for the preparation of colloidal solutions shows that a red or blue hydro-sol of copper is obtained, depending upon the properties of the solutions.

In G. Bredig's<sup>3</sup> method of producing colloids electrolytically, he obtained finely divided metallic gold, dark purple in color, when the arc takes place under distilled water. If a trace of caustic soda is added, deep red color is obtained.

That copper and gold are in the same condition in glass as in solutions is proven by the use of the ultra-microscope.

Zsigmondy<sup>4</sup> says that ruby glass will become red, or remain colorless upon slow cooling according to its quality. It will always remain colorless on chilling, the normal red color generally being brought out upon reheating to the softening point; (high lead glasses show yellow or brown instead of red). The coloring is due to the gold, which is at first homogeneously dissolved in

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<sup>1</sup> V. Pöschl, *Chemistry of Colloids*, p. 55.

<sup>2</sup> *Ibid.*, p. 66.

<sup>3</sup> *Ibid.*, p. 67.

the glass, later separating out in the form of ultra-microscopic particles which reflect green light.

He compares this phenomenon with devitrification, and refers to Tammann's<sup>5</sup> work on devitrification. Tammann shows that the speed of crystallization, and the ability to crystallize increase with diminishing temperature from the melting point and then decrease again, while viscosity steadily increases. Zsigmondy applies Tammann's results to ruby glass in this manner:

"Ruby glass is worked several hundred degrees lower than its melting temperature. At the working temperature, conceive it as a super-saturated crystalloid solution of metallic gold and the smallest amicroscopic particles to be centers of crystallization, it will at once be seen why ruby glass sometimes remains colorless upon simple cooling. In this case the optimum temperature for spontaneous crystallization is so low that the glass is very viscous and the speed of crystallization reduced to a minimum. If by reheating, the glass acquires a certain mobility, the gold separates out upon the nuclei present which by growth become sub-microns, visible in the ultra-apparatus and turning the glass red or darker."

V. Pöschl<sup>6</sup> says that gold ruby is obtained by an addition of gold chloride to the glass melt from which particles of gold separate out, when the mass is quickly cooled. These particles, however, have the magnitude of amierons, so that the glass appears colorless. By heating anew until the glass becomes soft, the particles grow until they attain the size of ultra-microns, to which the cause of the red color is traced. The preparation of copper ruby glass is performed by an analogous method.

Copper ruby has, in the past, been made by a process known as flashing. This process is described somewhat as follows by Rosenhain:<sup>7</sup>

"Flashing glass is the process of placing a very thin layer of colored glass on the surface of a more or less colorless glass of usual thickness. This is generally accomplished by taking a small gathering of the colored glass on the pipe, and the remaining gathering for the piece to be made from the colorless glass pot. When this glass is blown, the ruby glass lies in a thin layer over the inner surface of the cylinder. The special skill required is in blowing this layer to a uniform thickness to obtain a uniform color."

<sup>4</sup> Zsigmondy, *Colloids and the ultra-microscope*, p. 165.

<sup>5</sup> Tammann, *Zrit. for Electro-chemi*, 1904, Vol. 10, p. 532.

<sup>6</sup> *Ibid* I, p. 103.

<sup>7</sup> Walter Rosenhain, *Glass Manufacture*.

The necessity of flashing is due to the density of the color. Copper colors are so dense that many glasses are opaque when over 3 m.m. thick, the color depending upon the composition and rate of cooling. However, it is possible to control the density of the color somewhat in the flashed ruby glass by carefully controlling the temperature of working the glass and rate of cooling in the molds.

These factors must be controlled very carefully in practice to produce uniform results. If these glasses are cooled very quickly, as for instance, chilling in water or rolling very thin (2 m.m. thick) on an iron plate, the red color will not develop, or at least shows only in scattered streaks. By reheating at definite temperatures, the color may be obtained in varying degrees of intensity from amber to opaque black, depending upon the temperature to which the glass is reheated. Thus it will be seen that the temperature and rate of cooling must be constant, to produce a uniform shade of red when this color is developed during blowing.

At the present time, however, copper ruby glass is being made in which the color does not come out in the pressing or working, but is brought out later by reheating. The density of the color in this glass is very much less than the flashed ruby glass, and pieces of greater thickness can be easily made. The color range from a light amber through reds to a dense opaque black, with an increasing temperature.

Available literature consulted on the subject gave no complete or definite methods for working ruby glass, but emphasized the necessity for care.

The following are some formulae and directions obtained:

Gerner,<sup>8</sup> gives a history of copper ruby glass and a number of mixes with methods of handling. The following are two of the batches given by him:

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<sup>8</sup> Gerner, "*Glass*," p. 195.

## DEVELOPMENT OF RUBY COLOR IN GLASS

## GERMAN COPPER GLASS

100.0	Sand
25.0	Potash
17.0	Borax
2.5	Cu <sub>2</sub> O
5.0	SnO <sub>2</sub>
0.2	Fe <sub>2</sub> O <sub>3</sub>
2.5	MnO <sub>2</sub>
0.5	Bone ash

### Calculated Formula<sup>9</sup>

$$\left. \begin{array}{l} 0.200 \text{ PbO} \\ 0.390 \text{ K}_2\text{O} \\ 0.120 \text{ Na}_2\text{O} \\ 0.095 \text{ CuO} \\ 0.079 \text{ MnO} \\ 0.014 \text{ CaO} \end{array} \right\} \left. \begin{array}{l} 0.0060 \text{ Fe}_2\text{O}_3 \\ 0.2500 \text{ B}_2\text{O}_3 \\ 0.0044 \text{ P}_2\text{O}_5 \end{array} \right\} \left. \begin{array}{l} 4.36 \text{ SiO}_2 \\ 0.09 \text{ SnO}_2 \end{array} \right\}$$

## FRENCH COPPER GLASS

100 $\text{SiO}_2$	}	This batch is fused, chilled, dried, ground and mixed with 1 $\text{Cu}_2\text{O}$ , 1.5 $\text{SnO}_2$ , 5 cream of tartar. This is melted and blasted one hour during melt.
50 $\text{Pb}_3\text{O}_4$		
25 $\text{K}_2\text{CO}_3$		
5 $\text{NaNO}_3$		

### Calculated Formula

0.534 PbO	}	3.900 SiO <sub>2</sub>
0.346 K <sub>2</sub> O		
0.074 Na <sub>2</sub> O		
0.046 CuO		
		0.034 SnO <sub>2</sub>

Notes on ruby glass from Sprechsaal<sup>10</sup> give the following by translation:

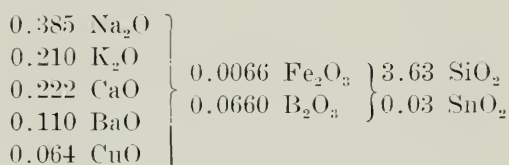
"In the manufacture of ruby glass it is not in the field of the furnace man to control the color. Repeated fusion and cooling makes the best color, and the color does not depend as much upon the percent of coloring oxide in the mix as upon the temperature of the glass while working, the rate of fusion and rate of cooling the finished piece." The following batch is given:

<sup>9</sup> The empirical formulae of all glasses given in the following work were calculated by the writer.

<sup>10</sup> *Sprechsaal*, Feb. 6, 1913, p. 92.

	LIGHT RED	DARK RED
Sand .....	100.0 kg.	100.0 kg.
Soda ash .....	16.0 kg.	16.0 kg.
Potash .....	16.0 kg.	16.0 kg.
Borax .....	4.0 kg.	6.0 kg.
Whiting .....	10.0 kg.	12.0 kg.
Witherite .....	10.0 kg.	10.0 kg.
Cu <sub>2</sub> O .....	2.0 kg.	4.0 kg.
SnO <sub>2</sub> .....	2.0 kg.	4.0 kg.
Fe <sub>2</sub> O <sub>3</sub> .....	0.5 kg.	1.0 kg.
Cream of tartar.....	0.8 kg.	1.3 kg.

## Calculated Molecular Formula

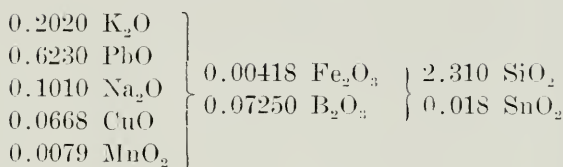


"The manufacture of ruby glass demands great care and practice in working. This is especially so with pressed glass. The raw batch should be put into a preheated pot and melted six hours. The melt is blasted several times and poured into cold water for remelting and refining. If the pressed pieces are not colored enough they can be reheated. The mold must not be too hot to allow the glass to cool too slowly, or too cold to chill and cause the pieces to crack. The following batch is also given:"<sup>11</sup>

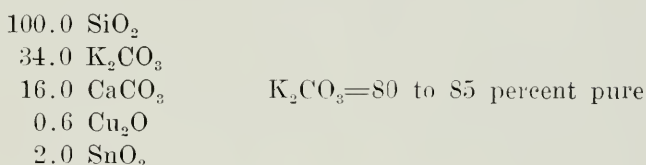
Sand .....	100.0 kg.
Potash .....	25.0 kg.
Red lead .....	25.0 kg.
Borax .....	10.0 kg.
Soda .....	5.0 kg.
Cu <sub>2</sub> O .....	3.5 kg.
SnO <sub>2</sub> .....	2.0 kg.
Fe <sub>2</sub> O <sub>3</sub> .....	0.5 kg.
MnO <sub>2</sub> .....	0.5 kg.
Cullet .....	25.0 kg.
Cream of tartar .....	0.5 kg.

<sup>11</sup> Ibid 10, p. 92.

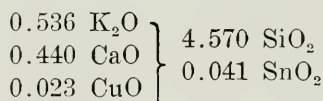
## Calculated Molecular Formula



Rudolf Hohlbaum<sup>12</sup> says that red colors may be obtained by the use of  $\text{Cu}_2\text{O}$ , selenium, sulphur and gold, but is most often obtained from  $\text{Cu}_2\text{O}$ . He gives the following batch for a copper ruby:



## Calculated Formula



Hohlbaum says:

"Concerning the mixing of the  $\text{Cu}_2\text{O}$ , I wish to remark that it is possible to obtain the ruby color with 0.4 percent  $\text{Cu}_2\text{O}$ , also with 0.8 percent. However, with 0.8 percent of the batch as  $\text{Cu}_2\text{O}$  the color is so dense that large masses are not workable. As such a small quantity of  $\text{Cu}_2\text{O}$  is needed to make ruby, it is mixed best by using 0.8 percent  $\text{Cu}_2\text{O}$  and  $\text{SnO}$  with half the batch of glass. When the glass is ready to blast then mix the batch containing 0.8 percent  $\text{Cu}_2\text{O}$  with an equal batch of crystal glass, and a 0.4 percent  $\text{Cu}_2\text{O}$  batch is obtained which gives a weaker color. It is best to employ  $\text{SnO}$  as a reducing agent to insure the obtaining of a ruby color, and one finds from practical experience that the mix must contain less than double the quantity of  $\text{Cu}_2\text{O}$  as  $\text{SnO}$ . If this is not sufficient reducing agent, cream of tartar may be used in quantities to satisfy all conditions. Iron scale may also be used as a reducing agent but the pure ruby color is then changed."

<sup>12</sup> R. Hohlbaum, *Seitgenasse Herstellung Bearbeitung und Verzierung des Feinern Hohlglases*, p. 125.



Hohlbaum<sup>13</sup> gives the following batch for a gold ruby:

#### Rose Color

Sand .....	100.0 kg.
Potash .....	34.0 kg.
Calcium carbonate .....	17.0 kg.
Gold .....	16.0 gms.

Gold must be brought into the mix in a very finely separated form, best in solution or as Purple of Cassius.

To get the gold in solution, it must be cut into small pieces and dissolved with aqua regia. The gold solution is poured on part of the mix, and this mixed with the balance of the batch.

In the heat of the oven, the decomposition of the gold chloride takes place so rapidly, that a portion of the gold chloride is carried away undecomposed. There is, therefore, not so much gold dissolved in the glass as is introduced, and the color is much weaker than it would be, if all the gold were dissolved. It is, of course, reasonable for one to try and reduce the vaporization of the gold chloride as much as possible. This may be done by pouring the gold chloride on 1 kgm. of sand and evaporating to dryness. Then mix this well with half of the batch, or use gold purple in the same manner.

According to Hohlbaum's experience, either phosphoric acid or barium work favorably in the making of gold ruby, causing the gold to separate out more rapidly. Without either, the ruby is too light. A batch for making a rose glass with a violet tinge with the use of barium is given.

#### Rose Glass with Barium

Sand .....	100.0 kgm.
BaCO <sub>3</sub> .....	16.0 kgm.
93 percent soda, Na <sub>2</sub> CO <sub>3</sub> .....	43.0 kgm.
Gold .....	12.0 gms.

#### Selenium Ruby, Light and Rose Colored

Arsenic .....	200.0 gms.
Sand .....	100.0 kgm.
Potash, 80-85 percent .....	34.0 kgm.
CaCO <sub>3</sub> .....	17.0 kgm.
Selenium nitrate .....	120.0 gms.

<sup>13</sup> Ibid 12, p. 126.

In the reds with sulphur, one should not use the alkali sulphates, but only sulphur with charcoal as a reducing agent. The charcoal keeps the sulphur from combining with the soda and potash. In sulphur ruby, a great part of the sulphur vaporizes in the working. The melting glass foams vigorously, and therefore one should fill the pot only half full at first, and after the batch reaches quiet fusion, put in the second half.

Sulphur ruby is hard to make in uniform colors, and darkens in the muffle. It is not used for making higher grades of glass. Two batches for sulphur ruby are given:

	No. 1	No. 2
Sand .....	100.0 kgm.	100.0 kgm.
Soda .....	45.0 kgm.	45.0 kgm.
CaCO <sub>3</sub> .....	20.0 kgm.	20.0 kgm.
Flowers of sulphur .....	7.0 kgm.	10.0 kgm.
Antimony sulphate .....	5.0 kgm.	
Charcoal .....	2.0 kgm.	

#### EXPERIMENTAL DATA BY WRITER

The foregoing typical batches for ruby glass are but a few of a large number given in the literature pertaining to glass making. An examination of these shows a wide variation in composition, but all agree in that they are high in silica and contain tin. In copper ruby, the amounts of copper and tin vary widely in their ratios to each other. These copper rubies are probably used in the manufacture of flashed glass.

In the beginning of the following experimental work, samples of commercial copper ruby, both the quick-cooled colorless and ruby colored were obtained. The uncolored sample was broken into fragments, and different fragments were heated to different temperatures for various lengths of time. A small Hoskins electric furnace was used, and temperatures were read with a Leeds Northrup potentiometer, using a platinum, platinum-rhodium thermocouple.

The following results were obtained:

TABLES

PIECE NO.	MAXIMUM TEMPERATURE	TIME HELD AT MAX. TEMP.	REMARKS
	$^{\circ}\text{C}$	<i>minutes</i>	
1	500	30	No change in color
2	500	60	No change in color
3	550	30	No change in color
4	550	60	No change in color
5	575	1	No change in color
6	575	30	No change in color
7	600	1	Very light amber
8	600	15	Very light amber
9	600	30	Bright amber, slightly darker than No. 8
10	600	60	Bright amber, same as No. 9
11	650	1	Bright amber, same as No. 9
12	650	30	Deep ruby, edges slightly softened
13	650	60	Same as No. 12, edges slightly softened
14	675	15	Same as No. 12, edges slightly softened
15	675	30	Same as No. 12, edges slightly softened
16	675	60	Darker than No. 15, edges slightly softened
17	700	1	Same as No. 10, edges slightly softened
18	700	30	Dark red, edges slightly softened
19	900	30	Grayish purple, opaque, softened out of shape

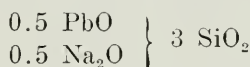
The rate of increase of temperature was a constant factor in all of these tests, as follows: ten minutes from room temperature to  $300^{\circ}\text{C}$ ;  $300^{\circ}\text{C}$  to  $500^{\circ}\text{C}$  at rate of  $50^{\circ}$  per minute;  $500^{\circ}\text{C}$  to maximum temperature at a rate of  $25^{\circ}$  per minute.

The results seem to show that the color at any definite temperature is practically constant, and that the color change at that temperature is apparently instantaneous. However, time is

required for the temperature to even up through-out the thickness of the piece.

It will be noticed that the glass shows signs of softening at that temperature at which the strong color develops. This is probably the softening point Zsigmondy<sup>14</sup> refers to in the article previously quoted. It is observed that there is little or no apparent change in color brought out between 650° and 675°, giving a safe range for an annealing oven.

Most of the glass formulas observed were high in lead and in silica. Accordingly the following formula was selected, it being the upper silica limit for most glasses:



In order to determine a suitable method of working, several small batches of this glass were fused. The method adopted was as follows:

The glass was fused in Battersea crucibles in a small pot furnace using gas and compressed air. The temperature range required for firing and to make the glass liquid enough for pouring, was between 1480°C and 1520°C. One-half hour was taken for complete fusion of the lead glasses and one hour for the leadless glasses.

Not much trouble was experienced in reducing the copper oxide and preventing oxidation. Although a slight reducing flame was used, the presence of cream of tartar (about 1½ percent) seemed to make reduction certain, if the time of heating was not too long.

When fusion was complete the glass was poured on a heavy cast iron plate 1 in. thick, and then rolled to a thickness varying from 2 to 5 m.m. The thinner portions usually cooled colorless, and the color developed in the thicker, slower cooled portions, i. e. turning red or opaque brown or black.

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<sup>14</sup> *Ibid* 4.

## FORMULAS

MATERIAL.	SERIES A GLASS NO.							SERIES A <sub>1</sub> GLASS NO.				
	1	2	3	4	5	6	7	1	2	3	4	
	0.50 0.50 ..... 3.00 0.04 0.04 0.50	0.500 0.500 ..... 3.000 0.004 0.004 0.500	0.500 0.500 ..... 3.000 0.004 0.010 0.500	0.500 0.500 ..... 3.000 0.002 0.007 0.500	0.500 0.500 ..... 3.000 0.001 0.007 0.500	0.500 0.500 ..... 3.000 0.0005 0.007 0.500	0.500 0.500 ..... 3.000 ..... 0.007 0.500	0.500 0.500 ..... 3.000 0.004 0.010 0.500	0.500 0.300 0.200 3.000 0.003 0.010 0.500	0.500 0.300 0.200 3.000 0.002 0.010 0.500	0.500 0.300 0.200 3.000 0.002 0.010 0.500	0.500 0.300 0.200 3.000 0.002 0.010 0.500
..... ..... ..... ..... ..... ..... ..... Cream of tartar, percent	..... ..... ..... ..... ..... ..... ..... .....	..... ..... ..... ..... ..... ..... ..... .....	..... ..... ..... ..... ..... ..... ..... .....	..... ..... ..... ..... ..... ..... ..... .....	..... ..... ..... ..... ..... ..... ..... .....	..... ..... ..... ..... ..... ..... ..... .....	..... ..... ..... ..... ..... ..... ..... .....	..... ..... ..... ..... ..... ..... ..... .....	..... ..... ..... ..... ..... ..... ..... .....	..... ..... ..... ..... ..... ..... ..... .....	..... ..... ..... ..... ..... ..... ..... .....	..... ..... ..... ..... ..... ..... ..... .....

## BATCH WEIGHTS

	SERIES A					SERIES A <sub>1</sub>				
	35.3 57.0	35.30 57.00	35.300 57.000	35.3000 57.0000	35.30000 57.00000	35.30 57.00	35.300 57.000	35.3000 57.0000	35.30 57.00	35.300 57.000
Na <sub>2</sub> CO <sub>3</sub> .....	35.3	35.30	35.300	35.3000	35.30000	35.30	35.300	35.3000	35.30	35.300
Pb <sub>2</sub> O.....	57.0	57.00	57.000	57.0000	57.00000	57.00	57.000	57.0000	57.00	57.000
White lead.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
CaCO <sub>3</sub> .....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
Flint.....	90.0	90.00	90.000	90.0000	90.00000	90.00	90.000	90.0000	90.00	90.000
Cu <sub>2</sub> O.....	1.4	0.14	0.070	0.035	0.018	0.14	0.070	0.035	0.14	0.070
SnO <sub>2</sub> .....	3.0	0.30	0.75	0.052	0.052	0.75	0.052	0.052	0.75	0.052
Cream of tartar.....	1.0	1.00	1.000	1.0000	1.00000	1.00	1.000	1.0000	1.00	1.000

## SERIES A

Glass batches were then made corresponding to the formulas given in Series A.

The following results were obtained:

Number 1—Colored out very dense opaque grayish-brown color.

Number 2—(Decreasing the coloring agent.) This poured well, and cooled practically colorless at 5 m.m. thick. Softened out of shape at 675°C. and colored out, streaked with reddish color. At 700°C. it became dark brown, opaque and still streaked, very soft.

Number 3—(Increasing tin to harden.). This poured well and was colorless except for a pale greenish-yellow color at 5 m.m. thick.

Heated to 480°C. gives amber color.

Heated to 525°C. gives deep red color.

Heated to 700°C. softened out of shape giving a dense, brown opaque glass. Color change very rapid.

Number 4—(Decreasing the  $\text{Cu}_2\text{O}$  to reduce intensity of color). Color developed darker than No. 3 in pouring, having a greenish cast. Heated to 600°C. its color was deep opaque, and nearly black, amber at 550°C., and brown at 575°C.

Number 5—Developed a rather intense brown color while pouring. Thin colorless sections gave a deep greenish brown at 550°C. and a dense opaque black at 600°C.

Number 6—(Still reducing amount of coloring matter). This glass poured clear and colorless. On reheating it changed to opaque black from 550°C. to 600°C. Color change very rapid.

Number 7—(Coloring matter left out to test purity of materials for iron). This glass on reheating at various temperatures gave no change in color.

The conclusions from this series of glasses, (excluding No. 1)<sup>15</sup> are:

(1) Low amounts of copper seemed to increase the density

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<sup>15</sup> This glass was not melted well enough to judge results.

or opacity of the color, and decrease the signs of red, giving greenish browns.

(2) An increase in the tin in No. 3 stopped the streakiness shown in No. 2.

(3) Glass No. 3 was the best glass in series A, giving a colorless glass when poured and cooled quickly. Reheating showed shades of good red at various temperatures. However, the color change is so rapid, it would be difficult to control uniformity of color.

### SERIES A1

Series A<sub>1</sub> was constructed in order to obtain harder glasses than those in series A, by replacing PbO with CaO so as to raise their temperatures of softening, and to determine how this affects the range of color change.

Glass No. 1 of this series showed a dark brandy color on pouring, coloring out quicker than No. 3 series A, which contained the same equivalents of Cu and Sn. This glass did not soften out of shape on reheating at 700°C., as did glass No. 3, series A, but gave a dense opaque color. If it could be handled, without coloring in pressing, this glass gives a good transparent red at 5 m.m. thick, upon reheating to the proper temperature.

Glasses Nos. 2 and 3 (reducing Cu<sub>2</sub>O). Colored out quite dense, on pouring becoming nearly opaque. When reheated above 600°C. the glass turned a deep opaque purple.

Glass No. 4 (reducing SnO<sub>2</sub>). This glass seemed to color out as rapidly as Nos. 2 and 3.

The conclusion which may be drawn from this series is that the rapidity of precipitation, or growth of color is increased, instead of decreased, as would be expected by hardening the glass.

### SERIES B

The basal formula for this series is one of the published formulas given in Sprechsaal.<sup>16</sup> It is a high lead low silica glass, containing some borax and is a much softer glass than series A and A1.

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<sup>16</sup> Ibid 10.



FORMULAS  
Series B

GLASS NO.	$\text{Na}_2\text{O}$	$\text{PbO}$	$\text{K}_2\text{O}$	$\text{SiO}_2$	$\text{CuO}$	$\text{SnO}_2$	$\text{MnO}_2$	$\text{Fe}_2\text{O}_3$	$\text{B}_2\text{O}_3$	CREAM OF TARTAR <i>percent</i>
1	0.101	0.623	0.202	2.31	0.0668	0.018	0.0079	0.0042	0.0725	0.5
2	0.102	0.627	0.202	2.33	0.0670	0.018	.....	0.0042	0.0730	0.5
3	0.101	0.623	0.202	2.31	0.0668	0.018	0.0079	.....	0.0725	0.5
4	0.102	0.627	0.202	2.33	0.0670	0.018	.....	.....	0.0730	0.5
5	0.102	0.627	0.202	2.33	0.0670	.....	.....	.....	0.0730	0.5
6	0.102	0.627	0.202	2.33	0.0670	.....	.....	0.0042	0.0730	0.5
7	0.101	0.623	0.202	2.31	0.0668	.....	0.0079	0.0042	0.0730	0.5
8	0.119	0.627	0.202	2.33	0.0500	0.018	.....	.....	0.0730	0.5
9	0.129	0.627	0.202	2.33	0.0400	0.018	.....	.....	0.0730	0.5
10	0.139	0.627	0.202	2.33	0.0300	0.018	.....	.....	0.0730	0.5
11	0.098	0.627	0.202	2.33	0.0710	0.018	.....	.....	0.0730	0.5
12	0.092	0.627	0.202	2.33	0.0770	0.018	.....	.....	0.0730	0.5
13	0.102	0.627	0.202	2.33	0.0670	0.023	.....	.....	0.0730	0.5
14	0.102	0.627	0.202	2.33	0.0670	0.067	.....	.....	0.0730	0.5
15	0.102	0.627	0.202	2.33	0.0670	0.134	.....	.....	0.0730	0.5

The results showed this very markedly. The fusions, made at the same temperature range  $1480^{\circ}\text{C}$  and  $1520^{\circ}\text{C}$ , were more fluid and poured easier.

Numbers 1, 2, 3 and 4 developed deep opaque glasses when poured 4 to 5 m.m. thick. The thinner portions, however, increased in degree of transparency to about 2 m.m. at which thickness the glasses cooled colorless, but of course very brittle. Upon reheating, the colorless pieces of these four glasses colored to about the same color density when heated to the same temperature. At  $500^{\circ}\text{C}$ , they showed an amber color changing to a light red at  $525^{\circ}\text{C}$ ., and to a ruby color at  $550^{\circ}\text{C}$ ., becoming opaque at  $600^{\circ}\text{C}$ . Leaving out the iron, or manganese or both, (especially the latter), seemed to improve the quality of the red and to give a less dense color. This type of glass gives a much better red color than any of series A, but it is impossible to work with sections as thick as commercial glass pieces would be made and still obtain a transparent color. However, it would work as a ruby glass in making flashed articles and give a good color. Manganese dioxide and  $\text{Fe}_2\text{O}_3$  are detrimental rather than helpful in obtaining good colors.

In series B, Numbers 5, 6 and 7 (in which  $\text{SnO}_2$  is absent), the glasses were more opaque in all cases. Number 7 colors out even in the thin sections to a dense black.

In glasses Nos. 8, 9, 10, 11 and 12, the tin was kept constant and the copper varied. In all cases the tendency was to increase opacity and the rapidity in which the color appeared on pouring.

In glasses Nos. 13, 14 and 15, in which the tin was increased, no beneficial results were obtained, since these glasses were more opaque than the preceding ones in the group.

The ruby color in glasses as soft, and as low in  $\text{SiO}_2$  as the members of this group cannot be controlled. However, when B1 and B2 were melted, quenched in water and remelted, there was an improvement, since all signs of streakiness disappeared, and the color became very uniform on reheating.

BATCH WEIGHT  
Series B

GLASS NO.	FLINT	POTASH	WHITE LEAD	BORAX	SODA ASH	$\text{Cu}_2\text{O}$	$\text{SiO}_2$	$\text{Fe}_2\text{O}_3$	$\text{MnO}_2$	CREAM OF TARTAR <i>percent</i>
1	100	26.0	30	10	13.2	3.50	2.00	0.5	0.5	1.0
2	100	26.0	30	10	13.2	3.50	2.00	0.5	...	1.0
3	100	26.0	30	10	13.2	3.50	2.00	...	0.5	1.0
4	100	26.0	30	10	13.2	3.50	2.00	...	...	1.0
5	100	26.0	30	10	13.2	3.50	...	...	...	1.0
6	100	26.0	30	10	13.2	3.50	...	0.5	...	1.0
7	100	26.0	30	10	13.2	3.50	...	0.5	0.5	1.0
8	100	26.0	30	10	17.2	2.60	2.00	...	...	1.0
9	100	26.0	30	10	18.8	2.10	2.00	...	...	1.0
10	100	26.0	30	10	20.6	1.56	2.00	...	...	1.0
11	100	26.0	30	10	12.4	3.70	2.00	...	...	1.0
12	100	26.0	30	10	11.2	4.03	2.00	...	...	1.0
13	100	26.0	30	10	13.2	3.40	2.55	...	...	1.0
14	100	26.0	30	10	13.2	3.40	7.45	...	...	1.0
15	100	26.0	30	10	13.2	3.40	14.90	...	...	1.0

The basis of this series obtained from Hohlbaum<sup>17</sup> is entirely different than series B. It is a lime-potash, high silica, leadless glass, with high tin, therefore, a comparatively refractory and viscous glass at low temperatures. One hour was taken for fusion.

Hohlbaum's batch calls for SnO as the reducing agent, cream of tartar being added as a precaution to insure sufficient reduction. Number C-I was first made by substitution of SnO<sub>2</sub> for SnO, and leaving out the cream of tartar. An oxidized clear colorless glass was the result, giving no color change when reheated beyond the softening point.

Number C-I was again made using SnO<sub>2</sub> and 0.5 percent cream of tartar. This glass was exceedingly viscous and quickly cooled below the point of easy pouring. Upon pouring and rolling, (although taking a little more time), no color change took place, the glass remaining clear and colorless.

Upon reheating, no color change took place until

800°C. was reached, when a light amber color was obtained,

850°C. gave a pale reddish brown,

900°C. gave a light brown,

1000°C. softened with an opaque brown color.

The red color was not good in this glass and it seemed to be entirely too refractory.

Series C, No. 2. (Reducing SiO<sub>2</sub> to soften). This showed an improvement in the working qualities with no tendency to color out on pouring.

Reheating this glass gave the following results:

800°C. a distinct light red,

850°C. a good ruby color,

900°C. a deep dark red nearly opaque when 4 m.m. thick.

Series C, No. 3 (reducing SiO<sub>2</sub> still further) gave a fusion which poured colorless and flowed freely. Reheated to 850° it showed a reddish brown, slightly streaked. 900° showed a distinct deep brown.

<sup>17</sup> Ibid 11, p. 125.

FORMULAS  
Series C

GLASS NO.	SiO <sub>2</sub>	K <sub>2</sub> O	CaO	CuO	SnO <sub>2</sub>	PbO	Na <sub>2</sub> O	B <sub>2</sub> O <sub>3</sub>	CREAM OF TARTAR
1	4.57	0.536	0.440	0.023	0.041	.....	.....	.....	0.5
2	4.00	0.536	0.440	0.023	0.041	.....	.....	.....	0.5
3	3.50	0.536	0.440	0.023	0.041	.....	.....	.....	0.5
4	3.00	0.536	0.440	0.023	0.041	.....	.....	.....	0.5
5	2.75	0.536	0.440	0.023	0.041	.....	.....	.....	0.5
6	4.57	0.536	0.240	0.023	0.041	0.200	.....	.....	0.5
7	4.00	0.536	0.240	0.023	0.041	0.200	.....	.....	0.5
8	4.00	0.536	0.340	0.023	0.041	0.100	.....	.....	0.5
9	4.00	0.536	0.340	0.023	0.041	.....	0.100	0.200	0.5
10	4.00	0.536	0.340	0.023	0.041	.....	0.100	.....	0.5
11	4.57	0.536	0.340	0.023	0.041	0.100	.....	.....	0.5
12	4.57	0.536	0.340	0.023	0.041	.....	0.100	.....	0.5

BATCH WEIGHTS

GLASS NO.	FLINT	POTASH	WHITING	Cu <sub>2</sub> O	SnO <sub>2</sub>	WHITE LEAD	SODA ASH	BORAX	CREAM OF TARTAR
1	200.0	68.0	32.0	1.2	4.46	.....	.....	.....	2.0
2	175.0	68.0	32.0	1.2	4.46	.....	.....	.....	2.0
3	153.0	68.0	32.0	1.2	4.46	.....	.....	.....	2.0
4	131.0	68.0	32.0	1.2	4.46	.....	.....	.....	2.0
5	120.0	68.0	32.0	1.2	4.46	.....	.....	.....	2.0
6	200.0	68.0	17.4	1.2	4.46	29.4	.....	.....	2.0
7	175.0	68.0	17.4	1.2	4.46	29.4	.....	.....	2.0
8	175.0	68.0	25.0	1.2	4.46	15.0	.....	.....	2.0
9	175.0	68.0	25.0	1.2	4.46	.....	.....	22.9	2.0
10	175.0	68.0	25.0	1.2	4.46	.....	10.4	.....	2.0
11	200.0	68.0	25.0	1.2	4.46	15.0	.....	.....	2.0
12	200.0	68.0	25.0	1.2	4.46	.....	10.4	.....	2.0

Series C, No. 4 (less  $\text{SiO}_2$  than C3). Poured clear and colorless but when reheated to  $850^\circ$  became more streaked and showed a more decided brown.

Series C, No. 5, poured clear and colorless as the others, but showed brown streaks. When reheated to  $800^\circ$  it showed a very streaked brown color. When the glass was remelted and repoured it gave a very clear glass.

Upon reheating this to  $750^\circ\text{C}$ . the color came out a clouded black, increasing in intensity with the reheating temperature.

The foregoing five glasses in group C show that:

(1) Reducing the  $\text{SiO}_2$  from 4.57 to 4.0 molecules improved the color in this series. Further reduction, however, changed the color to browns and then blacks, giving about the same range of brown and blacks with 3  $\text{SiO}_2$  as series A gave, having 3  $\text{SiO}_2$  and small amounts of copper.

(2) High silica seems necessary in order to develop a good red color. The color change takes place at rather high temperatures for a reheating furnace, and the glass appears to be too viscous for good working properties. Glasses C6, C7 and C8 were made by introducing  $\text{PbO}$  in place of part of the  $\text{CaO}$  with the idea of softening and, if possible, still retaining the property of not coloring out on pouring.

C6 and C7 in which 0.2  $\text{PbO}$  replaced 0.2  $\text{CaO}$  showed a distinct improvement in the working qualities and uniformity of color, although these glasses colored out in the thicker portions during the pouring; C6 to a light red and C7 to a deep ruby. These glasses, however, were transparent to a thickness of 8 m.m. in comparison with series B, which were not transparent in pieces over  $2\frac{1}{2}$  m.m. in thickness.

Reheating clear portions of C6 gave a good, deep, ruby color at  $650^\circ\text{C}$ ., a considerable lowering of the temperature over the leadless glasses for developing color. This glass also has a fairly constant color over a temperature range of  $25^\circ\text{C}$  ( $625^\circ\text{C}$ . to  $650^\circ\text{C}$ ).

Series C, No. 7 colored out at  $570^\circ$  to the same shade as C6.

Series C, No. 8 (Reducing  $\text{PbO}$  to 0.1 with 4.00  $\text{SiO}_2$ ). This glass gave evidences of being harder than the previous glass

(C7) as the fusion colored out a very little clearer at 6 m.m. thick (similar to C6), and the colorless portions gave a deep clear ruby on reheating to  $570^{\circ}$ , the same as C7 and about  $60^{\circ}$  lower than C6. This glass gave the clearest and best red obtained in the foregoing work.

Series C, No. 9 (in which 0.1 PbO was replaced in C8 by 0.1 Na<sub>2</sub>O as borax) gave a glass considerably more fusible, and flowed well in pouring. A very streaked, nearly black, color developed in portions over 3 m.m. in thickness on pouring. Thin transparent pieces heated to  $750^{\circ}$  gave a red color, streaked with opaque black lines. This fusion, therefore, did not give good results. The possibility of spoiling the color by over-heating is ever present. It is possible that less B<sub>2</sub>O<sub>3</sub> would give better results, though this was not tried.

Series C, No. 10 (0.1 Na<sub>2</sub>O replacing 0.1 CaO). The resulting glass was clear and colorless, showing a very few light red streaks. The working properties of the glass were very good, especially in pouring and cooling.

On heating to  $700^{\circ}\text{C}$  the glass turned a clear light red.

$625^{\circ}\text{C}$ . showed a clear light red.

$725^{\circ}\text{C}$ . showed a clear light red.

The color range of this glass is therefore good.

Series C, No. 11 (0.1 PbO replacing 0.1 CaO and with 4.57 SiO<sub>2</sub>). Results from this glass were a failure as the fusion was incomplete and very viscous and colored out a dense opaque black on pouring. If properly fused, better results would no doubt have been obtained.

Series C, No. 12 (0.1 Na<sub>2</sub>O replacing 0.1 CaO and with 4.57 SiO<sub>2</sub>). This glass gave a very good fusion, but was rather viscous and showed no color on pouring. Heating this glass to  $700^{\circ}\text{C}$  gave an amber colored glass streaked with dark red lines. At  $800^{\circ}\text{C}$  it showed a good even ruby color.

The conclusions from this last series of glasses (C6 to C12) are (1), that soda replacing lime softened the glass without causing the color to come out in cooling. (2) Lead on the other hand caused these glasses to color out rapidly on cooling, but did not make them opaque.



**General Conclusions.** The following are general conclusions one may draw from this work regarding the composition of a workable ruby glass. A workable ruby glass is one which will not color out when cooled at the rate obtained in the pressing process, and yet will give a workable range of temperature for reheating to a uniform color at temperatures below  $700^{\circ}$ .

1st. Highly fluid glasses will color out rapidly, viscous glasses slowly.

2nd. Replacing lime with either lead or soda, increases the rapidity of color development, lead more so than soda.

3d. High  $\text{SiO}_2$  is necessary for good color, low  $\text{SiO}_2$  gives a tendency towards brown or black, and opacity.

4th. High  $\text{SiO}_2$  (4.0 to 4.5 mol.), is necessary to give sufficient viscosity.

5th. With high silica, lime-potash glasses the tendency to streakiness increases. Small amounts of lead reduce streakiness.

6th. The glass giving the best color in series B is No. 4. Glasses Nos. 1, 2, 10 and 12 of Series C, most nearly approached the requirements of a good ruby glass. They could all be poured without the color developing, and on reheating, the color developed at favorable temperatures. Glasses Nos. 6 and 8, Series C gave the most transparent colors.

7th. Iron and manganese are detrimental to a good red color.

8th. Remelting improves the uniformity of the color which indicates that streakiness is due to lack of homogeneity.

9th. Density of color is apparently increased with an increase in temperature. Time is evidently not an important factor in this case.

## DISCUSSION

*Prof. Silverman:* There are a number of points in Mr. Williams' paper about which I wish to inquire. In the first place, he speaks of the coloring out in the high-silica copper rubies. I should like to ask whether Mr. Williams found any direct bearing by the alkali content of the glass. There is a claim

made at present that a copper ruby can be manufactured, which is a ruby, out of the pot. I believe his views correspond with mine in that the red color produced is due to high alkali in the glass. In other words, the glass colors out while cooling in the mold, or even earlier. Then as to tin as a reducing agent, I can corroborate these statements also, having had the experience that tin alone in connection with copper gives a rich color, while with manganese and iron the color is off. Tin has to be controlled very carefully. If you get below a certain point you obtain a glass which does not color sufficiently; and if you go above you get what is called clouding or a livery color.

I would like to ask, to what Mr. Williams attributes lack of uniformity of color; and whether he feels that a melt over a short duration, like thirty minutes could give a homogeneous glass.

*Mr. Williams:* To answer the last question first: the uniformity of color in my glasses was not obtained in the first melt. There were signs of streakiness at first, but upon remelting, good clear colors were obtained. It is probably the mechanical handling of the glass, or the duration of the melt which has a tendency to make the glass cloudy or clear.

The first question you asked, regarding the high alkali content, I did not quite understand, however I will make this point, that when I used lead, replacing the alkali, it caused the colors to come out more quickly in the handling. The color was just as good, in fact a little better, but density of color could not be controlled. Lead improved the uniformity of the color but gave a tendency toward opacity. If you do not want the color to come out during pressing, it is necessary to keep away from lead.

*Prof. Silverman:* I should like to know further, what the object is in trying to prevent the color from coming out during pressing.

*Mr. Williams:* If you do not prevent it, the different variations in the cooling of the mold would not give the same shading of red in the finished pieces.

*Prof. Silverman:* But do you not get the same effect by heating to a certain temperature afterwards?

*Mr. Williams:* Yes; but can you control the rate of cooling of glass in the mold sufficiently accurately as to give uniformity of color from piece to piece?

*Prof. Silverman:* I cannot quite see how that has a bearing on the rate of cooling. Suppose your glass does not color out below  $700^{\circ}$ . You might have a mold anywhere from  $400^{\circ}$  to  $600^{\circ}$ , and the fact that you have no color would be no indication that your mold temperature is correct. In other words, you have such a large range below the coloring-out temperature that it does not seem any better indication as to mold temperature, than if you had a glass that colored out, except possibly to tell you that the mold is too hot.

*Mr. Williams:* My experience with glass that colored out was that glass of various thicknesses was different in shade. The difference in temperature of a mold would influence the color. The coloring out at a definite temperature also depends upon the speed at which a glass cools through the small temperature range of color development. If the glass cools at a high rate of speed through this temperature, the colloidal copper would not come out in large enough particles to show color. If the cooling rate is slower the particles grow of sufficient size to give color.

*Mr. Gelstharp:* I should like to ask whether that was not sub-oxide of copper.

*Mr. Williams:* I used cuprous oxide.

*Prof. Stull:* Perhaps I might throw a little light on Prof. Silverman's question by stating, that among the things Mr. Williams is investigating is a study of the temperatures at which the copper ruby comes out, and the effect of length of time as well as temperature in bringing it out. That is why he is trying to secure colorless glass to begin with.















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